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THE ELECTRONIC THEORY OF CHEMISTRY

AN INTRODUCTORY ACCOUNT

BY

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TO MY OWN TEACHER
PROFESSOR J. F. THORPE, C.B.E., F.R.S.

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PREFACE

The last ten or twelve years have witnessed enormous developments in the Electronic Theory of Valency, the effects of which are to be seen not only in investigations of the problems of valency and molecular structure as such, but in the broadening of our outlook on many of the major problems of Organic Chemistry such as those of the directive effect of substituents in aromatic substitution, tautomerism, and the addition of hydrogen and bromine to conjugated systems.

A great change has overtaken what may be described as the *Classical Chemistry* on which most of us were brought up, accompanied by only very slight changes in nomenclature. The original papers containing most of the new ideas, such as the wave mechanical theory of the electron, are, unfortunately, quite incomprehensible to the ordinary Chemist. On the other hand, what is mostly required by those of us whose chemistry is of a vintage prior to 1922 is a working knowledge of the electronic theories in so far as they may be used to assist in the elucidation of chemical problems. In this connexion it is comforting to realise that despite the new quantum mechanical theories, the electron and the atom have not ceased to play their traditional rôles as discrete entities in our science, and that the results of wave mechanics analysis can be translated back into terms of the more familiar electronic models, on which the material of this book is based. There is still much to be said for the remark originally made by Professor J. F. Thorpe to the effect that if the Physicist had not conveniently provided us with the electron, the Chemist would have discovered it and called it by another name. Thus the theory of Lapworth, Robinson, and Ingold, that the influence of groups on the reactivity of organic molecules depends on electromeric displacements within these molecules, has recently received physical confirmation from Sutton's measurements of the dipole moments of benzene derivatives in relation to directive effect in aromatic substitution. Similarly it may be noted that Huckel's wave mechanical analysis of the structure of the benzene ring leads to what appears to be merely a more definite elaboration of the sextuple group theory of Robinson and Ingold, whose origin may be traced to the earlier writings of Bamberger towards the end of last century.

On the other hand, in developing the electronic theory of valency, we must, as Sidgwick has already emphasised, do our best to accept physical conclusions in full and avoid giving grounds for the old gibe that " when a Chemist talks about electrons he uses a different language from the Physicist." In this book, the attempt has therefore been made to develop the electronic theory from the point of view of the chemical investigator whose interest is mainly that of a " means to an end " in dealing with chemical problems, without committing any gross breach in relation to the views of modern physicists.

This book contains, in more extended form, the substance of the course of Seminar lectures on this subject which were delivered at Aligarh in April 1931, and is primarily intended for Honours degree students of Chemistry who intend proceeding to the M.Sc. and Ph.D. degrees of British and Indian universities.

In compiling this work I wish, however, to take this opportunity of expressing my own and very great indebtedness to the writings of Lewis, Sidgwick, Haas, Sugden, Lapworth, Robinson, and Ingold.

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FOREWORD

As the author states in his preface, the general acceptance of the electronic theory of valency during the past twelve years has brought about a profound change in our outlook on a great many chemical problems. The first major triumph of the electronic theory lay in the explanation it gave of the laws of valency in relation to the periodic classification of the elements. It incorporated into a single self-consistent viewpoint the three pre-existing partial theories of valency,—the electrochemical valency theory of ionising compounds, the non-polar valency theory of non-ionising compounds, and the co-ordination theory of molecular compounds. It gave a satisfactory general explanation of inorganic chemical properties, especially in relation to ionic and atomic dissociation and combination. Incidentally, it showed that a large number of accepted molecular constitutions required alteration; and subsequent experiment always proved the suggested modifications to be correct.

The second great success of the electronic theory lies in the field of organic chemistry. The first approximation conception which underlies the interpretation of all organic formulæ as expressions of reactivity, namely, that the chemical character of an organic molecule is the sum of the characters of its parts, is a commonplace of the introductory teaching of the subject; but, if it were true, organic chemistry would indeed be simple! We begin almost at once to teach that the additive principle is never strictly true that deviations occur everywhere and are often so great as to mask completely the general rule. The advanced study of organic chemistry has hitherto consisted largely in an empirical survey of these extremely complex deviations; and now for the first time the electronic theory has furnished a rational and general interpretation which can with confidence be applied throughout the whole field of organic chemistry.

In surveying the advances of the past twelve years, it is extremely satisfactory also to note that contemporaneously with the recognition of all this mass of *a posteriori* justification for the electronic theory, its physical foundations have been strengthened and deepened first by Heitler and London's theory of the bond, and secondly by the development of that theory in the hands of Slater and Pauling.

Thus, if not a revolution, at least a reformation on the grand scale has overtaken the conceptual basis of both inorganic and organic chemistry. A new rationale has been created, and it is most desirable that the inculcation of a proper appreciation of the historical aspects of chemistry should not be allowed to displace from chemical teaching the advantages of the more consistent and logical presentation which the recent developments have permitted.

This being the case, Professor R. F. Hunter has rendered a notable service to all teachers of chemistry in writing a general textbook from the modern viewpoint. The range of phenomena surveyed is very wide, and it is clearly the main theme of the book that a single consistent theory can illuminate many different fields of inorganic and organic chemistry. The writer is certainly to be congratulated on this timely and well-balanced production which will, we may hope, see many future additions as the subject advances.

C. K. INGOLD.

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THE ELECTRONIC THEORY OF CHEMISTRY

AN INTRODUCTORY ACCOUNT

CHAPTER I

THE FUNDAMENTAL PHYSICAL THEORY OF THE ELECTRON AND THE ATOM

The discovery of the *electron* as the negative atom of electricity and the universal constituent of all matter in the early part of the present century, led naturally to early speculation with regard to the electrical nature of chemical forces, but no serious progress in the development of the modern theory of valency could be made previous to Lord Rutherford's discovery of the nuclear atom in 1911. This originated in the observation that although positively charged α-particles are normally capable of passing through layers of metallic atoms with scarcely appreciable deflexion, they are occasionally deviated from their path by an extremely strong force of repulsion. Since electrical forces are inversely proportional to the square root of the distance, Rutherford concluded that α-particles which had been subjected to large deflexions of this type must have come into contact with something possessing a strong electrical repulsion, and a mass much closer to that of the α-particles themselves in magnitude, than the negatively charged electrons of the metallic atoms whose mass was known to be of the order of $\frac{1}{1840}$ of that of a hydrogen atom. This could only be a positively charged portion of the metallic atom, whose volume, in view of the infrequency of the phenomenon, must be small compared to that of the volume of the metallic atom. Rutherford therefore concluded that an atom contains a positively charged nucleus, occupying only a small portion of the volume of the atom, in which almost the whole of the mass was concentrated. Since the atoms of the elements are electrically neutral, it followed from this that the positive charge on the nucleus must be neutralised by surrounding electrons, which were assumed to be in a state of rotation of the type necessary to provide a stable system.

In 1913, it was discovered by Moseley that when the square roots of the frequencies of the characteristic X-rays produced from the cathode-ray bombardment of different elements were plotted against the ordinal numbers of the elements in the Periodic system (H = 1, He = 2, Li = 3, B = 5, etc.), a straight-line graph was obtained. These numbers, which Moseley termed the *atomic numbers* of the elements, are the numbers of the units of positive electricity in the nuclei of the elements. The atomic number of an element is therefore at once its ordinal number on the basis of the Periodic system, the number of positive charges on the nucleus, and the number of electrons surrounding the positive nucleus in the neutral atom. For the majority of the heavier elements, the atomic number has been deduced from Moseley's relationship, but in the case of hydrogen and helium, it has been deduced from the deflexion of the nuclei of these elements in electrical and magnetic fields. More recently, the atomic numbers of several elements deduced from Moseley's law have been confirmed by Chadwick's determination of the atomic number of metals by the deviation produced in passing α-particles through thin sheets of metallic foil.

The hydrogen atom possesses one electron, and the hydrogen nucleus whose charge is one quantum of positive electricity must therefore be regarded in a manner similar to the electron, as the unit of positive electricity, which is termed the *proton*, and with which nearly the whole of the mass of the hydrogen atom is concentrated. The fact that protons, like electrons, are the universal constituent of all the elements is proved by the artificial disintegration of atomic nuclei, since Rutherford has shown that degradations of this type always give rise to the emission of streams of hydrogen nuclei. It must therefore be concluded that all the atoms of the different elements are built up of electrons and protons.

With the exception of hydrogen, however, it will be observed that the atomic number of an element is usually, roughly, half its atomic weight. Since it is only the protons of the atom which contribute appreciably to its mass, it must therefore be concluded that the atoms contain in addition to their planetary electrons, *nuclear* electrons which are present so as to neutralise the excess of positive charge produced by the protons which are necessary to give the element its atomic weight. This can be illustrated by the case of fluorine, the atomic weight of which is 19, and the nucleus of which must therefore contain 19 protons to give the halogen this atomic weight. On the other hand, the atomic number of fluorine is 9, so that its nucleus must therefore contain 10 electrons to neutralise the excess of positive charge left over by the planetary electrons. Nuclear electrons are, of course, much more firmly held than planetary electrons and only manifest themselves as the β-rays of radio-active change.* Planetary electrons, on the other hand, are comparatively easily removed and are responsible for the phenomenon of ionisation.

The existence of nuclear electrons also supplies the clue to the explanation of the existence of isotopes. The positive charge on the nucleus of an atom determines the number of planetary electrons and also to a large extent the nature of their orbits. This means that the chemical and physical properties of an element are determined by its atomic number. If therefore we suppose that the same number of protons and electrons are added to the nucleus of a particular atom, a new atom will be obtained of greater atomic weight than the original, but possessing an identical system of planetary electrons. In other words, a new atom will be obtained of different atomic weight, but having chemical properties and physical properties in so far as they are not concerned with weight, identical to those of the first; that is, an isotope of the original element.

Accepting the theory of the nuclear atom, the first problem with which we are confronted is the nature of the relationships which govern the building up of the planetary systems of the atoms of the different elements of the Periodic table, and this can only be dealt with by reference to the *universal constant* which was introduced into physics by Planck in 1900 in connexion with the problem of radiation from black bodies, under the name of the "elementary quantum of action." Five years later, Planck's conception of the atomic structure of radiation was developed by Einstein, who showed that light behaves as though it consisted of small particles which he termed " light quanta," whose energy content is determined by the product of the elementary quantum of action and the frequency of light. In 1913, Bohr applied these ideas to Rutherford's model of the nuclear atom of hydrogen.

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* New light has been shed on this subject by the recent discovery of the *neutron*, which apparently possesses unit mass and no charge and may for certain purposes be regarded as a proton and electron fused together. If there are neutrons, it is no longer necessary to postulate the existence of free electrons in the nucleus, and the fact that the atomic weight is usually about twice the atomic number may be interpreted by saying that there are about equal numbers of protons and neutrons in the positive atomic nucleus.

Now Rutherford's picture of the hydrogen atom as consisting of an electron moving in an orbit round a positive nucleus was unsatisfactory, because under such conditions, the electron would be continuously accelerated towards the centre of its orbit, with a continuous loss of energy in the form of radiation, which would presumably come to a standstill only when the hydrogen atom had radiated all its energy and the electron and proton came into contact with each other. Bohr therefore made the assumption that the electron rotating round the hydrogen nucleus was stable only when the electron occupied one of a series of *fixed orbits*—the so-called " stationary states "—in which it was possible for the electron to rotate round the nucleus without losing energy in the form of radiation. These stable orbits were defined by a simple rule involving the elementary quantum of action, in which the angular momentum of the electron is always an integral multiple of Planck's constant $/2\pi$. He furthermore assumed that the hydrogen atom gives out energy in the form of radiation only when the electron jumps from one stable orbit to another, when the energy is liberated in the form of monochromatic radiation whose frequency is defined by the relation : $hv = E_2 - E_1$, where h is the elementary quantum of action, v the frequency of the light emitted, and E_2 and E_1 are the energies of the stable orbits concerned. This relation which leads to the Balmer formula for the hydrogen lines in the spectrum enabled Bohr to produce convincing evidence in favour of his theory in the calculation of all the frequencies of the hydrogen spectrum in excellent agreement with the experimental figures. Bohr furthermore showed that his theory leads to a most successful prediction of the value of the Rydberg constant ; the difference between the calculated value and the experimental value being less than the uncertainty of the values of the constants used in making the calculation.

The fundamental tenet of Bohr's theory is, however, the idea of more than one state of energy for an atom ; or as we now term it, more than one *energy level* defined by an integral multiple called the *quantum number*. In complex atoms, for instance, we may have several electrons all moving in orbits of their own, but all characterised by the same quantum number *n*, and all possessing, therefore, the same energy level. In the hydrogen atom, for instance, the innermost level for which the quantum number is 1, represents the *most stable* state for the atom. When the hydrogen atom becomes "excited" in an electrical discharge tube, this electron in the innermost orbit may be ejected into another outer "stationary" orbit. Sooner or later, however, it returns to the innermost and most stable orbit, and it may do this at one jump, or in several jumps between intermediate fixed orbits. As a result of this, hydrogen gas in a discharge tube exhibits hydrogen atoms in different states of excitement, resulting in a series of monochromatic rays which correspond to the transitions between the different energy levels.

The case of the hydrogen atom is, of course, comparatively simple, since we have to deal with a system consisting of a nucleus and one attendant electron. When we come to the more complex atoms, in which several electrons are rotating round a nucleus, the problem is much more serious and the methods of mathematical analysis unfortunately break down. On the other hand, we can work the application of Bohr's calculations for the hydrogen atom backwards, and from the experimental regularities observed in the spectra of different atoms, proceed to deduce their structure. This method of attack has had a remarkable degree of success and is the reason for the present prominence of spectroscopy in the investigation of chemical problems.

Bohr has assumed that all atoms contain a series of energy levels analogous to those of the hydrogen atom. If this is correct, then it is clear that there will be two kinds of planetary electrons in the more complex atoms, namely, electrons occupying innermost levels and which can only be removed under the influence of very strong forces such as those which are present in the production of X-ray spectra, and more labile electrons, occupying the outer levels which are more readily disturbed and raised to higher levels with the production of ordinary optical spectra.

The study of the X-ray spectra of the heavier elements indicates that planetary electrons can be divided into several groups. One electron, for instance, describing a one-quantum path, another a two-quantum path, and another a three-quantum path, and so on. For historical reasons, the one-quantum group has been called the K group, the two-quantum group the L group, the three-quantum group the M group, and so on.

Spectroscopy has shown that in the spectra of the more complex elements, the important lines in the optical spectrum fall into series which have been described as the Principal, Sharp, Diffuse, and Fundamental series. The theoretical explanation of this multiplicity indicates that the electrons whose transitions give rise to these spectral lines can exist in various states which are not accounted for by the K, L, M, etc., quantum numbers which are now termed *principal* quantum numbers. These transitions, which are concerned essentially with the angular momentum of the electron, are taken account of by what is termed the *subordinate quantum number.* These two quantum numbers are not, however, sufficient to account for all the lines of the spectrum of complex elements. Two further quantum numbers are necessary for this purpose which are concerned with the magnetic properties of the electron. These are known as the "spin quantum number," which takes account of the spin of the electron and is of fundamental importance in the development of the wave-mechanical theory of covalency formation, and the "magnetic quantum number," which is necessary to account for the resolution of spectral lines in a magnetic field.

As has been pointed out by Haas,[1] the necessity of four quantum numbers for the description of the motion of an electron is easily understandable on the basis that a complete description of electronic motion requires three co-ordinates, the rotation possessing three degrees of freedom, and the fourth degree of freedom arising from the spin of the electron round its own axis.

The allocation of the quantum numbers of an electron is limited by an important rule called "Pauli's Exclusion Principle," which provides the key to the understanding of the Periodic system on the basis of the quantum theory. This principle, which was discovered by Pauli in 1925, states that we *cannot have two electrons with the same four quantum numbers in any one atom.*[2]

If the K-, L-, M-, and N- groups of electrons are divided into sub-groups according to their subordinate quantum numbers, calling them Sub-group *s*, Sub-group *p*, and so on, the following are obtained for the maximum numbers of electrons in each sub-group:

Sub-group *s*	2 electrons
Sub-group *p*	6 electrons
Sub-group *d*	10 electrons
Sub-group *f*	14 electrons

A one-quantum K-group can contain only the sub-group *s*; an L-group can contain only the *s*- and *p*- sub-groups; an M-group the *s*-, *p*-, and *d*-sub-groups, and so on. From which it is deduced that the following are the greatest number of electrons which are possible in the different quantum groups:

One-quantum group K	2 electrons
Two-quantum group L	8 electrons
Three-quantum group M	18 electrons
Four-quantum group N	32 electrons

This leads at once to a scheme of atomic structure for the lighter elements which accounts very well for the periodicity of their chemical properties.—Thus the K level is filled at helium, and the next electron in lithium therefore enters the L level. The L level becomes filled at neon, and when we come to sodium the M level is therefore commenced by the next electron. The energy levels for the elements up to argon are shown in the following table:

Element	*Atomic Number*	*K Level*	*L Level*	*M Level*
H	1	1		
He	2	2		
Li	3	2	1	
Be	4	2	2	
B	5	2	3	
C	6	2	4	
N	7	2	5	
O	8	2	6	
F	9	2	7	
Ne	10	2	8	
Na	11	2	8	1
Mg	12	2	8	2
Al	13	2	8	3
Si	14	2	8	4
P	15	2	8	5
S	16	2	8	6
Cl	17	2	8	7
A	18	2	8	8

When we come to the next element, potassium, the M level can still hold another ten electrons, but it is assumed that the next electron enters the N level. This is of course in accordance with the chemical properties of potassium, but in addition to this, spectroscopic evidence makes it essential for the new electron to occupy the N energy level. Similarly, the electrons of calcium are distributed as follows: K level, 2; L level, 8; M level, 8; N level, 2.

After calcium, however, we come to the *transition elements*, whose position in the scheme of atomic structures so far outlined requires some explanation. These elements differ from the others in that they are capable of exhibiting divalency and trivalency, whereas the valency of ordinary elements usually varies by two units. Furthermore, they are frequently paramagnetic and they give rise to coloured ions. Lewis originally suggested that these properties were due to the presence of loosely held electrons which were capable of occupying more than one position in the electronic structure of these atoms. Bohr developed this suggestion in somewhat greater detail on the basis of the maximum number of electrons which can occupy a certain energy level. As has already been pointed out, after the completion of the octet at argon, the single additional electron of potassium, and the two additional electrons in calcium, take up positions in the N level despite the fact that there is still room for another ten electrons in the M level. At the next element, scandium, however, the additional room in the M level commences to be filled up; the structure of this element being: K level, 2; L level, 8; M level, 9; N level, 2. With titanium and vanadium, additional electrons are added to the M level, the outer valency group containing only two electrons. At chromium, however, a change takes place in that the M level contains thirteen electrons, and the N level contains only one electron. Chromium, as is well known, gives rise to divalent and trivalent ions, and it is therefore assumed that in the production of these, the second and third electrons are removed from the M level. The process of filling up the M level then continues until copper is reached, which has the structure (2)(8)(18)(1); the production of the cupric ion necessitating the removal of an electron from the M level. Beyond this element, the building up of the octet present in the krypton continues in the manner of the first short period of Mendeleef.

From the ease with which the higher valency ions are produced from the atoms of the transition elements, it must be concluded that the electrons necessary for this process can be removed from the M level in these elements with almost the same ease as they are removed from the outer N-level orbit. A point which gives still further emphasis to the extraordinary stability of the octet as compared with the other quantum groups of the Periodic system. This is of fundamental importance in the system of atomic structure in that the outer group of planetary electrons in all inert gases, with the exception of helium, contains eight electrons. The well-known insensitivity of these substances towards chemical reagents suggests an extraordinary degree of stability, which receives confirmation from the high ionisation potential of these gases, which is a measure of the work necessary to remove an electron from these stable groupings. The implication that the octet is associated with a high degree of stability is indeed very largely the basis of the modern electronic theory of valency.

It is therefore seen that the scheme of atomic structures which has been deduced from quantum principles enables us to account for the regularities of the Periodic System, and leads to a fundamental comprehension of the relation between atomic structure and chemical behaviour.

THE ELECTRONIC STRUCTURE OF THE ATOMS OF THE ELEMENTS

	Atomic	*Number of Electrons in the Electronic Levels*					
Element	*Number*	*K*	*L*	*M*	*N*	*O*	*P Levels*
H	1	1					
He	2	2					
Li	3	2	1				
Be	4	2	2				
B	5	2	3				
C	6	2	4				
N	7	2	5				
O	8	2	6				
F	9	2	7				
Ne	10	2	8				
Na	11	2	8	1			
Mg	12	2	8	2			
Al	13	2	8	3			
Si	14	2	8	4			
P	15	2	8	5			
S	16	2	8	6			
Cl	17	2	8	7			
A	18	2	8	8			
K	19	2	8	8	1		
Ca	20	2	8	8	2		
Sc	21	2	8	9	2		
Ti	22	2	8	10	2		
V	23	2	8	11	2		
Cr	24	2	8	12	1		

	Atomic	*Number of Electrons in the Electronic Levels*					
Element	*Number*	*K*	*L*	*M*	*N*	*O*	*P Levels*
Mn	25	2	8	13	2		
Fe	26	2	8	14	2		
Co	27	2	8	15	2		
Ni	28	2	8	16	2		
Cu	29	2	8	18	1		
Zn	30	2	8	18	2		
Ga	31	2	8	18	3		
Ge	32	2	8	18	4		
As	33	2	8	18	5		
Se	34	2	8	18	6		
Br	35	2	8	18	7		
Kr	36	2	8	18	8		
Rb	37	2	8	18	8	1	
Sr	38	2	8	18	8	2	
Y	39	2	8	18	9	2	
Zr	40	2	8	18	10	2	
Nb	41	2	8	18	12	1	
Mo	42	2	8	18	13	1	
Ma	43	2	8	18	14	1	
Ru	44	2	8	18	15	1	
Rh	45	2	8	18	16	1	
Pd	46	2	8	18	18	1	
Ag	47	2	8	18	18	1	
Cd	48	2	8	18	18	2	
In	49	2	8	18	18	3	
Sn	50	2	8	18	18	4	
Sb	51	2	8	18	18	5	
Te	52	2	8	18	18	6	
I	53	2	8	18	18	7	
Xe	54	2	8	18	18	8	
Cs	55	2	8	18	18	8	1
Ba	56	2	8	18	18	8	2
La	57	2	8	18	18	9	2
Ce	58	2	8	18	19	9	2
Pr	59	2	8	18	20	9	2
Nd	60	2	8	18	21	9	2
Il	61	2	8	18	22	9	2
Sa	62	2	8	18	23	9	2
Eu	63	2	8	18	24	9	2
Gd	64	2	8	18	25	9	2
Tb	65	2	8	18	26	9	2
Ds	66	2	8	18	27	9	2
Ho	67	2	8	18	28	9	2
Er	68	2	8	18	29	9	2
Tu	69	2	8	18	30	9	2
Yb	70	2	8	18	31	9	2
Lu	71	2	8	18	32	9	2
Hf	72	2	8	18	32	10	2
Ta	73	2	8	18	32	11	2
W	74	2	8	18	32	12	2
Re	75	2	8	18	32	13	2

	Atomic	*Number of Electrons in the Electronic Levels*						
Element	*Number*	*K*	*L*	*M*	*N*	*O*	*P*	*Levels*
Os	76	2	8	18	32	14	2	
Ir	77	2	8	18	32	15	2	
Pt	78	2	8	18	32	17	2	
Au	79	2	8	18	32	18	2	
Hg	80	2	8	18	32	18	2	
Tl	81	2	8	18	32	18	3	
Pb	82	2	8	18	32	18	4	
Bi	83	2	8	18	32	18	5	
Po	84	2	8	18	32	18	6	
Eka-I	85	2	8	18	32	18	7	
Rn	86	2	8	18	32	18	8	
Eka-Cs	87	2	8	18	32	18	8	1
Ra	88	2	8	18	32	18	8	2
Ac	89	2	8	18	32	18	9	2
Th	90	2	8	18	32	18	11	1
U-X	91	2	8	18	32	18	12	1
U	92	2	8	18	32	18	13	3

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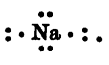
CHAPTER II

ELECTROVALENCY AND COVALENCY

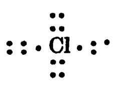
It is natural to assume that the external shells of electrons which are responsible for the stability of the inert gases, will confer stability on molecules as well as on separate atoms. The basis of chemical combination between atoms to give molecules may therefore be taken to be due to the tendency of the electrons in these atoms to assume more stable groupings than were possible in the separate atoms. With the exception of helium which contains only two electrons, all the inert gases possess an *octet* for their outer planetary system, and this plays a very important part in the development of the electronic theory of valency.

It is, of course, the electrons belonging to the outer belts of the planetary systems in atoms and possessing the highest principal quantum numbers, which are most susceptible to attack, for which reason they are commonly referred to as "valency electrons." With the exception of the transition elements, the number of valency electrons in an atom is given by the number of the group in the Periodic Table to which it belongs. Lithium, for instance, has one valency electron, carbon has four, nitrogen five, and so on.

In 1916, Kossel[1] in Germany and Lewis[2] in America independently made the suggestion that chemical combination between many elements arises from their tendency to gain or lose electrons from their outer valency belt in such a manner as to acquire the octet group present in the inert gases from neon onwards. Thus, if we consider the electronic structure of sodium and chlorine, it will be seen that the atom of sodium has an electron in its outer orbit, rotating round the closed L-group of eight electrons which is present in all elements of this period, while chlorine has an outer valency group of seven electrons.

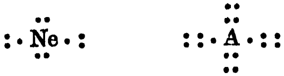


$$:\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Na}}}\cdot:\,.$$

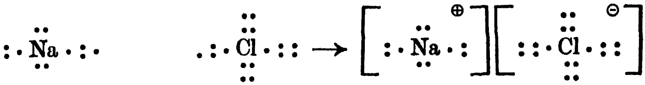


$$::\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}}}\cdot:\cdot$$

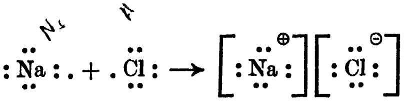
If sodium can therefore eliminate its odd electron in some way, it will acquire the stable electronic group of neon, and similarly if chlorine can acquire an electron it will be enabled to form the stable valency group of argon.



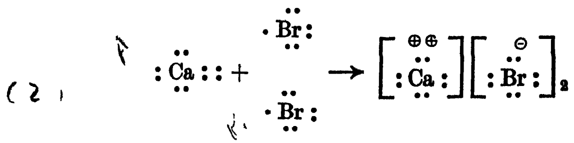
What therefore happens when these two elements come into contact is that sodium gives up its odd electron to chlorine, thereby becoming the positively charged sodium *ion*, and chlorine acquires argon-stability by becoming the negatively charged chlorine *ion* by the entry of this 8th electron into its M level. The products of interaction of sodium and chlorine are therefore the respective ions of these elements which are held together in the compound NaCl by electrostatic attraction.



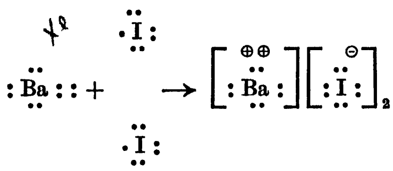
We can represent this more simply by taking account only of the electronic orbits which are actually concerned in the change:



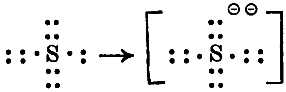
The formation of calcium bromide from calcium and bromine may be visualised as a transfer of the two electrons of the N level in calcium to the outer valency groups of the two bromine atoms; calcium thereby reverting to the argon type of structure by becoming the divalent positive calcium ion, and the bromine atoms completing their octets and acquiring the stable valency group of krypton by becoming univalent negative bromine ions:



Similarly, the formation of barium iodide from barium and iodine consists in the transference of the two electrons of the P level in barium to the iodine atoms, whereby both barium and iodine acquire the stable valency group of xenon (2.8.18.18.8) by becoming the divalent positive barium ion and the univalent negative iodine ion respectively.



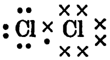
Sulphur contains an outer valency group of six electrons, that is two short of the number which it requires to obtain the octet of argon, which it readily takes up with the production of the divalent negative sulphide ion:



This is the essence of the electronic theory of valency put forward by Kossel some seventeen years ago,[1] which provides an excellent explanation of the formation of ionised compounds. The theory is to a certain extent a modern interpretation of the century-old electro-valent theory of Berzelius which had such a remarkable degree of success in explaining the behaviour of *ionised* inorganic compounds at the beginning and end of the Nineteenth Century. On the other hand, there are clearly many inorganic molecules such as those of hydrogen, oxygen, and chlorine in which it is impossible to say that one atom is charged positively and the other negatively, and furthermore it is evident that Kossel's theory is useless from the point of view of the Organic Chemist.

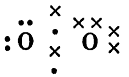
The clue to the nature of chemical combination which does not involve the production of charged ions was, however, given by Lewis in the same year. Lewis developed his theory of covalent linkages by means of a static cube model which is now of only historical interest, but his theory nevertheless was the genesis of the modern theory of *homopolar* bonds.

Lewis, like Kossel, assumed that chemical combination is the result of the tendency of electrons to redistribute themselves amongst atoms in such a way as to assume the stable valency groupings which occur in the inert gases, but he made the fundamental advance over Kossel in suggesting that it is possible for *an electron to be shared between two atomic nuclei in such a way as to contribute towards the stability of both.* Like Kossel, Lewis assumed that the chlorine atom which is an electron short of the M level of argon may acquire this by forming the negative chlorine ion of sodium chloride, but he also assumed that two chlorine atoms can complete their octets by mutually sharing an electron belonging to each:

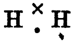


$$:\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}\overset{\times}{\underset{\bullet}{}}\overset{\times\times}{\underset{\times\times}{Cl}}\overset{\times}{\underset{\times}{}}$$

The fundamental point in Lewis's theory is that both octets are thus completed *without transference of electrons,* and therefore without the transference of charge. This type of valency bond, which was later named *covalency* by Langmuir, enables us to explain the existence of non-ionising molecules. The molecule of oxygen for instance, O_2, was interpreted as octet completion by the mutual sharing of four electrons between the nuclei,* while the existence of the hydrogen molecule is due to the formation of the stable *duplet* grouping of helium:

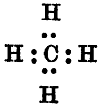


$$:\overset{\bullet\bullet}{O}\,\overset{\times}{\underset{\bullet}{\overset{\bullet}{\underset{\times}{}}}}\,\overset{\times\times}{O}\overset{\times}{\underset{\times}{}}$$

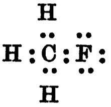


$$H\overset{\times}{\underset{\bullet}{}}H$$

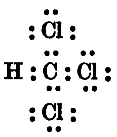
Methane, methyl fluoride, chloroform, and carbon tetrabromide are formulated such that the octets of carbon, fluorine, chlorine, and bromine are all completed by covalency sharing:



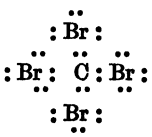
$$\begin{array}{c} H \\ H:\overset{\bullet\bullet}{\underset{\bullet\bullet}{C}}:H \\ H \end{array}$$



$$\begin{array}{c} H \\ H:\overset{\bullet\bullet}{\underset{\bullet\bullet}{C}}:\overset{\bullet\bullet}{\underset{\bullet\bullet}{F}}: \\ H \end{array}$$

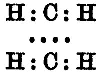


$$\begin{array}{c} \bullet\bullet \\ :Cl: \\ H:\overset{\bullet\bullet}{\underset{\bullet\bullet}{C}}:\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}: \\ :Cl: \\ \bullet\bullet \end{array}$$

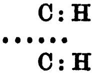


$$\begin{array}{c} \bullet\bullet \\ :Br: \\ :\overset{\bullet\bullet}{\underset{\bullet\bullet}{Br}}:\overset{\bullet\bullet}{\underset{\bullet\bullet}{C}}:\overset{\bullet\bullet}{\underset{\bullet\bullet}{Br}}: \\ :Br: \\ \bullet\bullet \end{array}$$

The electronic formulæ for ethylene and acetylene are obtained by replacing each valency bond in the ordinary formulæ for the compounds by an electronic duplet.



$$\begin{array}{c} H:C:H \\ \bullet\bullet\bullet\bullet \\ H:C:H \end{array}$$



$$\begin{array}{c} C:H \\ \bullet\bullet\bullet\bullet\bullet\bullet \\ C:H \end{array}$$

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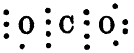
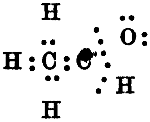
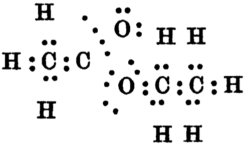
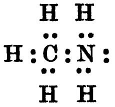
* It is now known, however, that this view of the structure of the oxygen molecule can no longer be maintained since the ground-level formula derived from its band spectrum indicates that there are two π-electrons in an unclosed group, whose spin is uncounterbalanced.

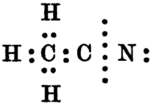
Similarly, the electronic formulæ for carbon dioxide, acetaldehyde, ethyl acetate, methylamine, and acetonitrile are as follows:



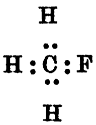


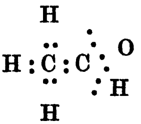


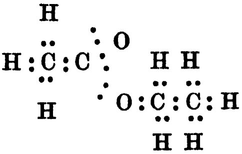




The application of Lewis's theory to carbon compounds is therefore particularly instructive, and the translation of the classical formulæ for most organic compounds into their electronic equivalents can generally be accomplished by writing an electronic duplet for each bond in the older formulæ and filling in the unshared electrons in the outer valency groups of the atoms concerned. This frequently leads to formulæ which provide an explanation of the behaviour of organic molecules which are not obvious on the basis of ordinary structural formulæ. In all these formulæ, only the outer electronic groups which are concerned in the building up of the molecules are considered, and for most purposes it is sufficient to consider only those electrons which are actually concerned in covalent sharing, and electronic pictures of this type



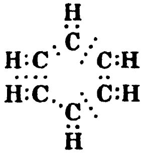


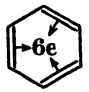


can generally be obtained merely by writing two dots for each valency bond in the classical formulæ. Exceptions to this rule are of course provided by the nitro compounds and other molecules containing semipolar double bonds which are discussed in the next chapter.

Particular interest attaches itself to the electronic formulation of the benzene nucleus. The translation of the more or less generally accepted Kekulé formula into terms of covalencies gives the picture (I), but a much more fundamental advance than this has recently been made by Huckel [3] by applying the principles of wave mechanics analysis to this outstanding problem of Organic Chemistry.

(I)





(II)

In the present state of our knowledge, anything in the nature of a complete quantum mechanical analysis of a molecule as complex as benzene is impossible, and Huckel has had to make a number of assumptions which may, or may not, be entirely justified. The starting-point in his analysis is that there are six electrons in the molecule over and above those required for joining carbon to carbon and carbon to hydrogen. By using certain approximations, the quantum states of these electrons can be worked out, and when Pauli's principle is applied, it is found that a system of six electrons constitute a "closed group," somewhat analogous to the closed groups in the Periodic system, and it is to this closed group that the manifestation of aromatic properties is attributed. Huckel has furthermore shown that a system of eight electrons does not constitute a closed group, and this of course accounts for the lack of aromatic properties in *cyclo*octatetraene. Huckel's theory of the benzene nucleus is indeed very largely a more definite elaboration of the sextuple group theory of Robinson [4] and Ingold [5] in which benzene is formulated as in (II), and whose origin can be traced to the earlier writings of Bamberger towards the end of last century. The position is probably best summarised by Hinshelwood's statement, that although quantum mechanics cannot solve the benzene problem at this stage, it at least gives us good grounds for believing that ring systems possessing a group of six electrons unaccommodated in single bonds possess unusual properties and stability

The fundamental difference between polar or electrovalent linkages and covalent linkages is that in the former, there is no real bond between the atomic nuclei composing the molecule. In the molecule of NaCl, the sodium ions and chlorine ions are merely held to one another by the force of electrostatic attraction which is overcome when the substance is dissolved in a solvent of sufficiently high dielectric constant. The formula NaCl for sodium chloride is indeed, in a sense, symbolically erroneous in that it implies that a particular sodium ion is associated with a particular chlorine ion in the solid state. Actually we know from Bragg's *X*-ray analysis of sodium chloride crystals that in the crystal lattice of the salt each sodium ion is surrounded by six chlorine ions, and each chlorine ion in turn is surrounded by six sodium ions, and that there is no reason whatever to suppose that one particular chlorine is more closely associated with one sodium than any of the other five. The molecules indeed are essentially agglomerations of ions, each keeping its electrons in the same state of binding as if it were isolated, and maintained in a prescribed structure by the operations of crystalline forces in conjunction with electrostatic attraction. In covalent compounds, on the other hand, quite another state of affairs obtains. In these compounds, the linking electrons or linking orbits form part of the constitution of both atoms concerned and count towards the stability of both. The positions of the atoms in space, relative to the linking orbits, is therefore fixed, and they cannot be altered beyond the limits of comparatively slight distortion without causing the rupture of the linkage. Covalencies thus possess definite directions in space and are therefore capable of producing *stereoisomerism* when the same sets of atomic nuclei are capable of more than one arrangement round a particular atom.

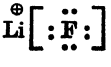
Although the Lewis theory has been used with a remarkable degree of success in dealing with many of the problems of Organic Chemistry, the nature of the covalency linkage—that is to say, how it is possible for two atomic nuclei to share electrons such that they contribute to the stability of both—has been one of the standing problems of the electronic theory of valency. It is only now that with the forging of the new mathematical weapon of wave mechanics by de Broglie, Schoedinger and Heisenberg, that it has been possible to throw some light on this fundamental problem of molecular structure.

From Pauli's principle and from the theory of electron spin to which reference was made in the previous chapter, it will be seen that there are two types of electrons in an atom—electrons which may be termed "corresponding" in that their principal, subordinate, and magnetic quantum numbers are identical, and others in which this is not the case. It follows from Pauli's principle that the spin quantum numbers of "corresponding electrons" must be different, and since the spin quantum number can have only two possible values, corresponding to "clockwise" and "anti-clockwise" rotation, it follows that corresponding electrons can occur only in pairs. It is a fairly obvious step to identify the number of unpaired electrons in an atom with its valency, and this is the essence of London's theory of covalency,[6] which in this sense reduces the problem of valency to a problem of the quantum theory. Covalency is explained as a neutralisation or coupling of the spins of the electrons belonging to the atoms which form the homopolar bond through resonance. The formation of the hydrogen molecule is for instance visualised as a union of two hydrogen atoms with oppositely spinning electrons. Since there are only two possible directions of spin, the saturation of chemical valencies becomes explainable on this basis. The formation of a covalency may therefore be regarded as being accompanied by a reduction of one unit of the resultant spin quantum number of the system, and according to London, therefore, when all the covalencies of an atom are saturated, the resultant spin quantum number of the system is zero. The carbon atom in methane, for instance, is considered to have its eight electrons disposed in the same manner as the stable closed group in neon.

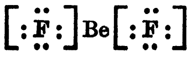
With regard to the operation of electrovalency and covalency in the Periodic table, it is instructive to examine the first short period of Mendeleef.

Periodic Group .	1	2	3	4	5	6	7	
Element . .	Li	Be	B	C	N	O	F	Ne
Atomic Number .	3	4	5	6	7	8	9	10
Valency Electrons	1	2	3	4	5	6	7	8

All these elements from lithium onwards have the inner group of K electrons, and their number of valency electrons is therefore two less than their atomic number in the Periodic table. It will be observed that they are hypothetically capable of acquiring electrons to form the neon structure, or giving up electrons and reverting to the stable group present in helium. As might be anticipated, it is found that the earlier elements of the series tend to lose electrons with reversion to the helium duplet, whilst the later elements take up electrons to acquire the neon octet. Thus we have the simple ions of lithium and beryllium containing the helium duplet and oxygen and fluorine ions containing completed octets:



$\overset{\oplus}{\text{Li}}[:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{F}}}:]$



$[:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{F}}}:]\text{Be}[:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{F}}}:]$

When the intermediate elements, *boron*, *carbon*, and *nitrogen*, are examined, however, it is found that they do not form simple ions, but that they readily combine with the atoms of other elements by means of covalency linkages. Now covalency linkages necessarily involve a gain of electrons and consequently carbon, nitrogen, and oxygen never revert to the helium structure, but always proceed towards neon in their attempt to complete their octets.

On the basis of this, an answer may be given to the old question as to whether hydrogen should be included with the alkali metals or with the halogens.—The alkali metals are typical univalent metals, possessing an electron more than the inert gas which precedes them, which is readily given up with the formation of positively charged ions. In this sense, hydrogen appears at first sight to bear a strong resemblance to the alkali metals in possessing an electron which is readily given up with the production of the proton. There is, however, a very definite difference between the cases in that hydrogen, unlike the alkali metals, possesses a strong tendency to form covalent links with the formation of ions of the type of the ammonium ion $[NH_4]^{\oplus}$, and the hydrated hydrogen ion $[H_3O]^{\oplus}$: present in aqueous solutions of mineral acids. The combination of hydrogen and chlorine differs, for instance, from that of sodium and chlorine in that the hydrogen chloride produced in the reaction is a non-conductor of electricity in the anhydrous state ; the link between hydrogen and chlorine being covalent :

$$H:H + :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \longrightarrow 2\,H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$$

The halogens, on the other hand, are typical univalent electronegative elements, having an electron less than that required for inert gas-group stability which they readily acquire with the formation of negative halide ions. It is possible for hydrogen to simulate them, however, by taking up an additional electron with the production of the *negative* hydrogen ion $[\cdot H\cdot]^{\ominus}$. This property of hydrogen was actually predicted by Lewis as far back as 1916, and has now received confirmation by the preparation of hydrides of lithium and calcium which possess the structures

$$Li[\cdot H\cdot]^{\ominus} \text{ and } Ca[\cdot H\cdot]^{\ominus}_2$$

and yield hydrogen at the *anode* on electrolysis.

It may be noted that the numerical value of the electrovalency of an atom is identical with its normal covalency. Thus, the electrovalency of an electronegative element, for instance, is the number of electrons which the atom requires for the completion of its octet. In the formation of a normal covalency, however, an atom always acquires a share in a new electron, so that chlorine, for instance, will therefore be univalent in both sodium chloride and methyl chloride.

The second short period of elements resembles in its essential features the first period. Thus the L level is completed in all these elements, and sodium therefore resembles lithium in containing an electron more than the inert gas which precedes it which is readily given up with the production of the sodium ion. Magnesium resembles beryllium in properties, silicon resembles carbon in its tetracovalency, and chlorine resembles fluorine in the ease with which it takes up the electron necessary to enable it to acquire octet stability by the formation of the chlorine ion.

With the third period, however, a new state of affairs obtains with the appearance of the transition elements, whose special properties have already been alluded to in Chapter I.

Element . .	K	Ca	Sc	Ti	V
Electronic Groups	2.8.8.1.	2.8.8.2	2.8.9.2	2.8.10.2.	2.8.11.2
			(2.8.8.3)	(2.8.8.4)	(2.8.8.5)

Element . .	Cr	Mn	Fe	Co	Ni
Electronic Groups	2.8.13.1.	2.8.13.2	2.8.14.2	2.8.15.2.	2.8.16.2
	(2.8.8.6)	(2.8.8.7.)	(2.8.13.3)	(2.8.14.3)	

These elements are characterised by the ease with which electrons can be removed both from the outermost group and the next innermost group of electrons, with the production of divalent and trivalent ions such as those of iron which may be written:

Fe'': K level, 2; L level, 8; M Level, 14 electrons.
Fe''': K Level, 2; L Level, 8; M level, 13 electrons.

With the filling up of the M level with the maximum number of electrons, the elements from copper to krypton resemble those of the first period with regard to outer electronic groups and therefore as regards chemical behaviour.

Element	Cu	Zn	Ga
Structure	(2.8.18.1)	(2.8.18.2)	(2.8.18.3)
Element	Ge	As	Se
Structure	(2.8.18.4)	(2.8.18.5)	(2.8.18.6), etc.

The octet of the N level being completed at krypton, electrovalency occurring at both ends of the period from facile loss or gain of electrons and covalency being manifested towards the centre of period as in arsine, whose structure is analogous to that of ammonia. There is of course the difference that the positive ions produced by the earlier elements of the period such as Cu′ and Zn″ possess an outer valency group of 18 electrons. Copper, it may be noted, differs from the rest of the elements of the period in resembling the transition elements in the formation of the divalent cupric ion which has the electronic structure (2.8.17), in addition to the univalent cuprous ion (2.8.18).

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1. Kossel, *Ann. d. Physik.*, **49**, 229, 1916.
2. Lewis, *J. Amer. Chem. Soc.*, **38**, 762, 1916.
3. Huckel, *Z. Physik.*, **70**, 204, 1931.
4. Armit and Robinson, *J. Chem. Soc.*, **127**, 1605, 1925.
5. Goss and Ingold, *J. Chem. Soc.*, 1928, p. 1268.
6. London, *Z. f. physik.*, **46**, 455, 1928.

CHAPTER III

THE CO-ORDINATE LINKAGE

Covalencies are produced by the mutual sharing of a pair of electrons between two atomic nuclei, A and B, in such a way that the electrons contribute towards the stability of both systems

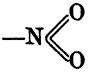
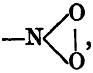
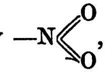
$$A \underset{\bullet}{\times} B$$

Suppose, however, that the atom A possesses a completed stable group in which two electrons are unshared, while the atom B possesses an outer group of electrons which is short of the stable number by two. The atom A could then share its *lone-pair* of electrons with the atom B covalently, such that the atom B, for instance, completes its octet while the stable grouping of the atom A is undisturbed.

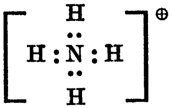
$$:\overset{\bullet\bullet}{\underset{\bullet\bullet}{A}}:\overset{\times\times}{\underset{\times\times}{B}}{}^{\times}_{\times}$$

This constitutes another means of forming a covalent link, which to distinguish it from *normal* covalency in which sharing is mutual, is termed *co-ordinate* covalency.

The fundamental difference between this type of linkage and normal covalency is the fact that the second atom B receives a share in two electrons originally belonging to the first atom A, with the result that it must acquire something in the nature of negative charge, whilst a compensating positive charge appears on the first atom. The formation of the co-ordinate linkage should therefore be accompanied by segregation of positive and negative electricity, or as we now term it *polarisation*, and is in a sense a process of *intramolecular ionisation.* Although the link between the atoms A and B is a single covalency, the second atom B increases the number of its shared electrons by two, and in a sense the linkage therefore corresponds to a double bond. For this reason it has been named a *semipolar double bond* by Lowry and Sugden, who represent it as $\overset{+}{A}—\overset{-}{B}$ and $A \mathrel{\overset{\rightharpoonup}{=}} B$, respectively; the half barb in the latter being in the direction of the atom which receives a share in the lone pair of electrons of the first. Sidgwick, on the other hand, terms this linkage a *co-ordinate covalency* and represents it by a full arrow in the direction of the atom which thus augments the number of its shared electrons, A ⟶ B. It must be emphasised at this point, however, that although this third variety of chemical linkage is necessary for the purpose of explaining the formation of a large number of compounds of a type which has attracted growing attention in recent years, the theory of the co-ordinate link lacks the sound physical background which has been provided for normal covalency by wave mechanics.

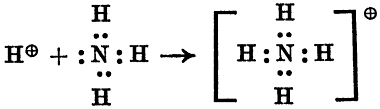
The application of the theory of the co-ordinate link is probably best illustrated by Sidgwick's treatment of the problem of the structure of the nitro group.[1] The L level in nitrogen contains five electrons, that is three short of the number required by the stable group present in neon, and the normal covalency of nitrogen is therefore three as in ammonia and the amines. The alternative formulæ suggested in the older textbooks of Organic Chemistry contain a "quinquevalent" nitrogen atom  $-N\begin{array}{l}\diagup\!\!\!\!\diagup O\\ \diagdown\!\!\!\!\diagdown O\end{array}$ or a three-membered heterocyclic ring  $-N\begin{array}{l}\diagup O\\ \;|\\ \diagdown O\end{array}$, which are open to objection from the point of view of the Octet Rule and the theory of stability of rings, respectively. The conception of the co-ordinate link, however, introduces a third possibility, namely  $-N\begin{array}{l}\diagup\!\!\!\!\diagup O\\ \searrow O\end{array}$, in which the second oxygen atom completes its octet by sharing the lone-pair of electrons of the nitrogen atom of the nitroso stage $R\,\colon\overset{\cdot\,\cdot\,\cdot}{\underset{\cdot}{N}}\colon O$. Measurement of the dipole moment of nitro compounds indicates a high and approximately constant degree of intramolecular ionisation for this group (see Chapter V), and Sugden's measurement of the parachor of a number of nitro compounds (see Chapter VI) lends support to the co-ordinate formula, which is now commonly used in English chemical literature. On the other hand, difficulties are presented by the fact that the introduction of a second nitro group *para* to that in nitrobenzene results in a zero dipole moment in *p*-dinitrobenzene. This formula for the nitro group is also open to serious objections from the point of view of Hund's[2] developments of the Heitler-London theory of covalency.

Sidgwick's theory of co-ordination provides, on the other hand, an excellent interpretation of the relationship between tervalent nitrogen and the so-called "pentavalent" nitrogen present in ammonium salts. The octet of nitrogen is completed by taking up three hydrogen atoms with the formation of ammonia, and the introduction of a further hydrogen atom would therefore give rise to an electron in excess of that required for the stable configuration of neon. This electron is therefore immediately eliminated with the production of the univalent positively charged ammonium ion:



$$\left[\begin{array}{c}\mathrm{H}\\ \mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}:\mathrm{H}\\ \mathrm{H}\end{array}\right]^{\oplus}$$

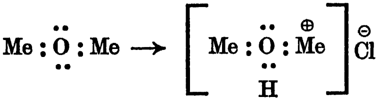
This does not differ materially from Lewis' interpretation of the formation of the ammonium ion by co-ordination of a proton with a molecule of ammonia:



$$\mathrm{H}^{\oplus} + \begin{array}{c}\mathrm{H}\\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}:\mathrm{H}\\ \mathrm{H}\end{array} \rightarrow \left[\begin{array}{c}\mathrm{H}\\ \mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}:\mathrm{H}\\ \mathrm{H}\end{array}\right]^{\oplus}$$

It will be noted that the *core* of the nitrogen atom is unaltered in both processes, and Sidgwick therefore emphasises that in this sense there is no real change of valency in passing from tervalent nitrogen to nitrogen in ammonium salts. The expulsion of the additional electron introduced by the fourth hydrogen atom is the condition whereby nitrogen acquires tetracovalency, and in so doing resembles tetracovalent carbon in methane. Actually, London has pointed out that the four original electrons of nitrogen which remain after the expulsion of the fifth which is taken up by the electronegative atom, can be assigned quantum numbers in the same way as the four electrons of the carbon atom in methane, such that the structure of the ammonium ion may be represented by a scheme of quantum numbers identical to that of methane. In accordance with this, the resolution of the ammonium ion by Mills and Warren [3] indicates that the four groups which are attached to nitrogen by non-electrovalent links in the ammonium ion, occupy the points of a tetrahedron in space, whilst the fifth group is not definitely attached to nitrogen but is merely held to the ammonium ion by electrostatic attraction.

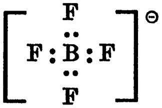
An explanation similar to this has also been advanced for the formation of oxonium salts. Oxygen completes its octet by covalent sharing with two methyl groups in dimethylether, and union with a hydrogen atom would therefore result in an electron in excess of that required for the stable grouping present in neon. If oxygen can eliminate an electron, however, it will increase its covalency by a unit and resemble nitrogen in ammonia and the amines. The formation of dimethyloxonium chloride which is presumed to exist in solutions of dimethylether in hydrochloric acid is therefore interpreted as the elimination of an electron from the outer group of electrons of the oxygen atom and covalent union with a hydrogen atom with the production of the positive oxonium ion and the negative halide ion:



$$\mathrm{Me}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{Me} \longrightarrow \left[\mathrm{Me}:\overset{\cdot\cdot}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{O}}}:\overset{\oplus}{\mathrm{Me}}\right]\overset{\ominus}{\mathrm{Cl}}$$

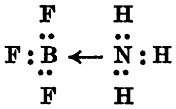
The formation of sulphonium ions and the iodonium ions present in the diaryliodonium salts first discovered by Victor Meyer is interpreted on similar lines.

Considerable interest attaches itself to the case of boron, however, because boron contains only three electrons in the L level and is therefore five short of the number required for the stable configuration of neon. It has therefore room for a further five electrons, but it cannot acquire quinquecovalency because it has only three valency electrons to offer for covalency formation. Boron therefore takes up three fluorine atoms with the production of boron trifluoride, and three methyl groups with the formation of boron trimethyl. In both of these compounds boron is two electrons short of its octet, and Sidgwick therefore interprets the formation of the negative borofluoride ion as completion of the octet by coordination of boron trifluoride with a negative fluoride ion:



$$\left[\mathrm{F}:\overset{\overset{\mathrm{F}}{\cdot\cdot}}{\underset{\underset{\mathrm{F}}{\cdot\cdot}}{\mathrm{B}}}:\mathrm{F}\right]^{\ominus}$$

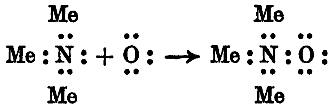
A similar explanation of the formation of the addition compound of boron trifluoride with ammonia, BF_3, NH_3, is also advanced by Sidgwick on the assumption that this compound owes its existence to the tendency for boron to complete its octet by co-ordination with ammonia by means of the lone pair of electrons of the tertiary nitrogen atom:



$$\begin{array}{ccc} \mathrm{F} & & \mathrm{H} \\ \mathrm{F : \overset{\bullet\bullet}{\underset{\bullet\bullet}{B}}} & \longleftarrow & \mathrm{\overset{\bullet\bullet}{\underset{\bullet\bullet}{N}} : H} \\ \mathrm{F} & & \mathrm{H} \end{array}$$

It must be pointed out, however, that difficulties are presented by the fact that boron trichloride forms a similar addition compound with ammonia of the composition $(BCl_3)_2(NH_3)_3$, and that there is no evidence of the formation of a $[BCl_4]^{\ominus}$ ion from boron trichloride by co-ordination with chlorine ion. An alternative explanation of the existence of such addition compounds is that their formation is due to an enhanced form of dipole association since the phenomenon occurs mainly in the First Period; due presumably to the small atomic dimensions of these elements.

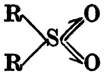
A somewhat similar explanation of the formation of the ammonium oxides, in which nitrogen has completed its octet at the tertiary stage, but still possesses its lone pair whereby it takes up an oxygen atom, enabling oxygen to complete its octet with the formation of a co-ordinate covalency.

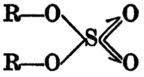


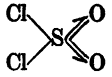
$$\begin{array}{ccccc} \mathrm{Me} & & & \mathrm{Me} & \\ \mathrm{Me : \overset{\bullet\bullet}{\underset{\bullet\bullet}{N}} :} & + & \mathrm{\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} :} & \longrightarrow & \mathrm{Me : \overset{\bullet\bullet}{\underset{\bullet\bullet}{N}} : \overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} :} \\ \mathrm{Me} & & & \mathrm{Me} & \end{array}$$

The compound is therefore now written either as $\mathrm{Me_3N} \stackrel{\rightharpoonup}{=} \mathrm{O}$ or $\mathrm{Me_3\overset{+}{N}{-}\overset{-}{O}}$.

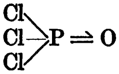
The "hexavalency" of sulphur in the sulphones, the esters of sulphuric acid, and in sulphuryl chloride is similarly attributed to the sharing of the two lone pairs of electrons of the M level of the sulphur atom with oxygen; the formulæ for these compounds being therefore:



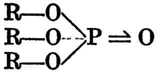




Phosphoryl chloride and the esters of orthophosphoric acid are similarly formulated with a single semipolar double bond between phosphorus and oxygen, the presence of which receives experimental confirmation from the parachor determinations of these compounds.[4]

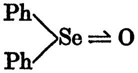


$\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\!>\!\mathrm{P} \rightleftharpoons \mathrm{O}$

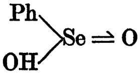


$\begin{matrix}\mathrm{R{-}O}\\\mathrm{R{-}O}\\\mathrm{R{-}O}\end{matrix}\!>\!\mathrm{P} \rightleftharpoons \mathrm{O}$

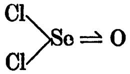
Similarly, the measurement of the parachors of diphenyl selenium oxide, phenyl selenious acid,[5] and selenium oxychloride indicates that selenium shares a lone pair of electrons with oxygen in each of these three compounds, whose formulæ are therefore:



$\begin{matrix}\mathrm{Ph}\\\mathrm{Ph}\end{matrix}\!>\!\mathrm{Se} \rightleftharpoons \mathrm{O}$



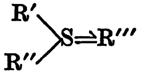
$\begin{matrix}\mathrm{Ph}\\\mathrm{OH}\end{matrix}\!>\!\mathrm{Se} \rightleftharpoons \mathrm{O}$



$\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\!>\!\mathrm{Se} \rightleftharpoons \mathrm{O}$

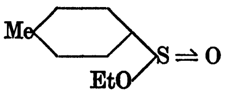
An interesting stereochemical confirmation of the existence of semipolar double bonds was provided almost simultaneously with Sudgen's parachor determinations of compounds of this type in 1925, by Phillips [6] by the resolution of esters of *p*-tolylsulphinic acid.

If the tetrahedral configuration for sulphur is accepted, it is seen that the groups R′, R″, and R‴ in compounds of the type



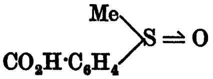
$\begin{matrix}\mathrm{R'}\\\mathrm{R''}\end{matrix}\!>\!\mathrm{S} \rightleftharpoons \mathrm{R'''}$

are not in the same plane as the sulphur atom, and the compounds should therefore be capable of exhibiting optical activity due to the presence of the semipolar double bond. This was confirmed experimentally by Phillips in 1925 by resolving ethyl-*p*-toluenesulphinate

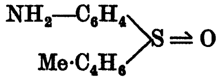


into isomeric forms having rotations of 16·5° and − 6·7° in alcoholic solutions.

In the following year, Harrison, Kenyon and Phillips [7] succeeded in resolving *m*-carboxyphenylmethylsulphoxide and 4′-amino-4-methyldiphenylsulphoxide into optically active forms in accordance with formulæ (I) and (II) respectively.

(I) 

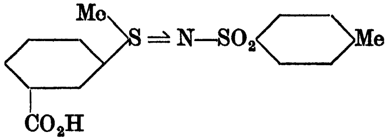
$\begin{matrix}\mathrm{Me}\\\mathrm{CO_2H{\cdot}C_6H_4}\end{matrix}\!>\!\mathrm{S} \rightleftharpoons \mathrm{O}$

 (II)

$\begin{matrix}\mathrm{NH_2{-}C_6H_4}\\\mathrm{Me{\cdot}C_4H_6}\end{matrix}\!>\!\mathrm{S} \rightleftharpoons \mathrm{O}$

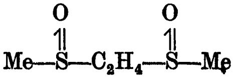
Important confirmation of these structures is provided by the oxidation of these compounds to sulphones, which involves the production of a second semipolar double bond with a consequent destruction of optical properties due to the fact that the molecules thereby obtain a plane of symmetry.

A similar phenomenon but involving lone sharing of sulphur with nitrogen has been provided by the case of the sulphonylimine (III), which has been isolated in stereoisomeric modifications possessing rotations of + and – 338° in alcohol.[8]



(III)

Geometrical isomerism of the *cis-trans* type has also been observed by Bell and Bennett [9] in compounds of the type of dimethylethylenedisulphoxide (IV) in which the oxygen atoms which are held by the semipolar double bonds to sulphur are not in the same plane as the other radicals forming the $R'R''S\,R'''$ complex.



$$\mathrm{Me{-}\overset{\overset{O}{\uparrow\!\!|}}{S}{-}C_2H_4{-}\overset{\overset{O}{\uparrow\!\!|}}{S}{-}Me}$$

(IV)

Compounds of this type are isolable in pairs of isomeric forms which can be recognised by means of their melting-points and crystalline form; the disulphoxide (IV), for instance, has been obtained in two forms, termed α- and β-, which have m.p.163–164° and 128–130° respectively.

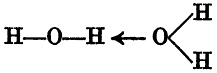
In connexion with the formation of co-ordinate links, the suggestion has been made by Sidgwick[10] and others, that although the stable group for the hydrogen atom is the duplet of normal covalency, in certain circumstances this is capable of expansion to a stable grouping of four electrons.

It is well known that hydrogen fluoride differs from the acids of the other three halogens in being polymerised even in the gaseous state, and in the formation of stable double salts of the type KHF_2. These facts point to the existence of molecules having the formula H_2F_2, giving rise to the univalent negative ion $[HF_2]^{\ominus}$. This ion is evidently produced by the combination of a molecule of hydrogen fluoride with the fluoride ion. Sidgwick assumes that fluorine does not co-ordinate with the fluoride ion, and that sharing takes place by co-ordination between the fluoride ion and hydrogen; the valency group of hydrogen being augmented to four in the complex ion:

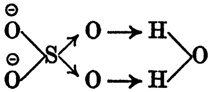
$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}: \qquad \text{or} \qquad [F \rightarrow H—F]^{\ominus}$$

The formula of the acid H_2F_2 being therefore $H[F \rightarrow H—F]^{\ominus}$.

The same author has also used this assumption of the expansion of the valency group of hydrogen to explain the polymerisation of water; co-ordination being assumed to take place by way of the lone pair of electrons of the oxygen atom:



A theory of anionic hydration has been developed on similar lines by Sidgwick; in which, for instance, the hydrated form of the sulphate ion is written:



All these suggestions are, however, open to very grave objections in the light of the physical theories discussed in Chapter I. Thus it is known that the K level cannot contain more than two electrons, because this would provide a contradiction to Pauli's principle in that it would necessitate two or more electrons in the atom having the same four quantum numbers.

It is therefore much more reasonable to suppose that the acid H_2F_2 and the ion $[HF_2]^{\ominus}$ owe their origin to some form of loose combination between fluorine ion and hydrogen fluoride, due to the known polarisation of the hydrogen fluoride molecule. The fact that this type of polymerisation and complex ion formation is restricted to the lowest member of this group is probably due to the fact that the interatomic distance in hydrogen fluoride (0·92 Å) is considerably smaller than that of the next member, hydrogen chloride (1·28 Å).[11] Similarly, the polymerisation of water is probably attributable to the definite dipole moment produced by covalent sharing of hydrogen and oxygen (p. 49), which would be expected to produce a type of " head and tail " self-neutralisation of water molecules leading to associated complexes of varying stability. It must be conceded, however, with regard to the former case that the existence of stable double salts of the K[HF_2] does suggest the manifestation of stronger forces than are usually mentally associated with the process of dipole association.

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10. Sidgwick, *The Electronic Theory of Valency*, London, 1929, p. 72.
11. Lennard-Jones, *Chemistry at the B.A. Centenary*, 1931, p. 218.

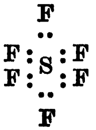
CHAPTER IV

COVALENCIES HIGHER THAN FOUR

Although the stable valency group in most cases is the octet which is present in the outer electron belt of all the inert gases with the exception of helium, there are a number of compounds in which, on chemical grounds, it seems reasonable to suppose that the valency group has been expanded to twelve and even to sixteen electrons.

It must be admitted at the outset that there is no definite physical basis for the assumption that a group of twelve electrons should possess unusual stability, such as exists in the case of the duplet and the octet, but covalencies higher than four are manifested by certain elements and appear to necessitate the assumption of the expansion of the valency group beyond its normal limit.

The most striking example of this is probably furnished by sulphur hexafluoride, SF_6. This compound, as is well known, is a gas of extraordinary stability which can be passed through water and even hot alkali without undergoing decomposition. It provides a striking contrast in its properties, to the higher halides of the type of phosphorus pentachloride and antimony pentachloride whose labile halogen atoms are assumed to be held by singlet linkages. The behaviour of sulphur hexafluoride is indeed very similar to that of carbon tetrachloride in respect to its stability towards hydrolysing agents. There are therefore strong grounds for supposing that the six fluorine atoms are held by normal covalencies, and that the compound has the formula:

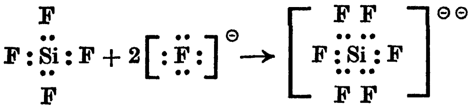


$$\begin{array}{ccc} & F & \\ & \cdot\cdot & \\ F: & S & :F \\ F: & \cdot\cdot & :F \\ & F & \end{array}$$

SF_6

Since sulphur possesses six valency electrons, this can only be accomplished by *expanding the outer valency group to twelve electrons*.[1]

A similar expansion of the octet in silicon tetrafluoride to a valency group of twelve electrons, appears to be the basis of the formation of the negative silicofluoride ion from this compound and fluoride ions:



$$\begin{matrix} F \\ F:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Si}}:F \\ F \end{matrix} + 2\left[:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:\right]^{\ominus} \longrightarrow \left[\begin{matrix} F\;F \\ F:\underset{\cdot\cdot\,\cdot\cdot}{\overset{\cdot\cdot\,\cdot\cdot}{Si}}:F \\ F\;F \end{matrix}\right]^{\ominus\ominus}$$

Actually hexacovalency does not represent the maximum covalency limit, since osmium gives rise to osmium octafluoride, OsF_8, but particular interest attaches itself to the phenomenon of hexacovalency in the light of the existence of the hexa-co-ordinated compounds of Werner.

It will be recalled that Werner's theory of co-ordination was first published in 1891, and more fully elaborated in 1893[2] in an attempt to explain the formation of the so-called "molecular" or "complex" compounds of Inorganic Chemistry, and more particularly, the compounds which are formed from inorganic salts and ammonia. The earlier attempts to explain the existence of substances of this type had been highly unsatisfactory, and Werner made the fundamental advance in suggesting that their production was due to the tendency of certain atoms to attach to themselves a definite number of atoms or groups, irrespective of whether these were univalent atoms or whole molecules capable of an independent existence. Werner termed the number of such atoms or groups, which are capable of being taken up in this way by a particular number, the *co-ordination* number of that atom. This number was sometimes four, but more often *six*, and the atoms or groups forming the whole complex were assigned to what were termed the "first" and "second spheres," according to the ease with which they could be removed from the co-ordination complex. The ammonia molecules in the hexamine of cobaltic chloride $[Co(NH_3)_6]Cl_3$, for instance were assumed to occupy the first sphere, while the chlorine atoms which are characterised by being ionised in water, were assigned to the second sphere. Werner was also responsible for the device of the square bracket for the purpose of distinguishing between these spheres, which is now commonly used to denote ionisation. The most important point in Werner's theory, however, was that he assigned a definite stereochemical configuration to the atoms and groups attached to the central atom of the co-ordination complex. The components of a 6-co-ordinated complex were given the configuration of the points of an octahedron; a suggestion which was subsequently confirmed by the resolution of asymmetric molecules of this type into optically active forms. Indeed, it was not until Werner had postulated the existence of stereochemical relations of this type in his co-ordination compounds and confirmed this experimentally, that his theory received the position to which it was clearly entitled in chemical science.

The following series of platinum amines, which have been taken from Sidgwick's "The Electronic Theory of Valency,"[3] is particularly instructing in that the position of the square bracket in the compounds has in every case been determined by experiment and the relative figures for the molecular conductivity at 25°, which are written below the formulæ, show that they are approximately proportional to the number of ions into which these compounds are dissociated in aqueous solutions:

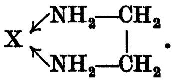
$[Pt(NH_3)_6]Cl_4$	$[Pt(NH_3)_5Cl]Cl_3$	$[Pt(NH_3)_4Cl_2]Cl_2$
(523)	(404)	(229)
$[Pt(NH_3)_3Cl_3]Cl$	$[Pt(NH_3)_2Cl_4)]$	$[Pt(NH_3)Cl_5]K$
(97)	(0)	(108·5)

In all these compounds, the co-ordination number is *six*, and the central platinum atom has always six groups, either NH_3 molecules or chlorine atoms . . . attached to it by covalent linkages, and it is interesting to observe that whenever a molecule of ammonia in the series is replaced by a chlorine atom, the complex loses a positive charge, its electrovalency falling by a unit if it is positive and rising by a unit if it is negative.

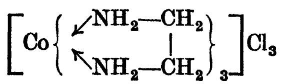
The essence of Werner's theory may therefore be summarised as follows: (i) the central atom has a definite number of atoms or groups attached to it, and this number which is usually six, has no relation to the periodic group of the central atom, (ii) the groups forming the co-ordination complex may be either univalent atoms or radicals, or whole molecules such as those of ammonia, and (iii) there is a change in electrovalency in the compound when a group belonging to one of these types is replaced within the complex by one of the other type. The translation of this into modern electronic terminology can be accomplished on the lines suggested by Sidgwick, on the basis that Werner's 6-co-ordinated compounds are produced by the expansion of the octet to a valency group of twelve electrons such as may be assumed to exist in sulphur hexafluoride.

In the first place, the links which join the atoms or groups of the co-ordination complex to the central atom are *covalent,* and the maximum co-ordination number is therefore the maximum covalency number. An atom which has a co-ordination number of 6 is therefore hexacovalent. The attachment of a univalent radical such as the nitro group or a chlorine atom involves the production of a normal covalency in which one electron is supplied by the radical and one by the central atom of the co-ordination complex. On the other hand, the attachment of a molecule of ammonia or water has a different significance, in that the incoming group brings with it its own pair of electrons for the formation of the co-ordinate link. The number of shared electrons of the central atom is the same whether the co-ordination units are molecules such as ammonia, or univalent radicals, and this explains why there is a change in electrovalency as radicals are exchanged for molecules, unit by unit. The process has been illustrated by Sidgwick with reference to the non-ionised compound $Pt(NH_3)_2Cl_4$. Suppose a neutral atom of chlorine is removed from this, it will take with it one of the electrons which were previously shared with platinum, but it will leave the other behind. If now a molecule of ammonia takes its place, this provides the two electrons required for the co-ordinate link between nitrogen and platinum, with the result that there is therefore an electron in excess of that required for the stable co-ordination complex. The system will therefore eliminate this, becoming positively charged and giving rise to salts of the type: $[Pt(NH_3)_3Cl_3]\overset{\ominus}{Cl}$.

In all the co-ordination compounds which have so far been mentioned in this book, each associating radical or compound has occupied one position in the co-ordination complex. There are, however, radicals and compounds which function as twofold associating groups, and the substances obtained in this way have played a very important part in the development of the co-ordination theory. These twofold units form rings containing the central atom of the co-ordination complex, and have been named *chelate* compounds (from χηλή for crab's claw) by Morgan and Drew.[4] Thus in certain co-ordination compounds a molecule of ethylenediamine (symbolised en) takes the part of two ammonia molecules in the co-ordination complex:



For instance, three molecules of ethylenediamine take the place of the six ammonia units in the compound $[Co(NH_3)_6]Cl_3$, with the production of the chelated derivative:



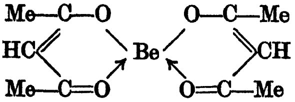
which is usually written: $[Co(en)_3]Cl_3$.

A point of historical interest in connexion with these chelate ethylenediamine derivatives is that it was by means of substances of this type that Werner first demonstrated the octahedral distribution of associating units in hexaco-ordinated compounds by resolution of compounds of the type:

$$[CoCl(NH_3)(en)_2]X_2,\ [CoCl(NO_2)(en)_2]X,\ \text{and}\ [Co(en)_3]X_3$$

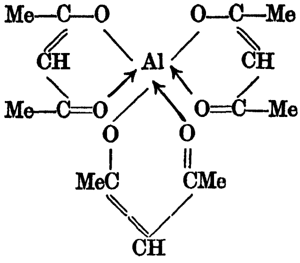
into optically active enantiomerides in 1911.

The stability of chelate compounds is of a relatively high order, due probably to the fact that the ordinary covalencies hold the molecule together even when the co-ordinate links are ruptured. Indeed, the metallic derivatives of β-diketones of the type of acetyl-acetone exhibit such remarkable stability that they can be fused, and frequently distilled without undergoing decomposition. These substances exhibit typical covalent properties, in that they dissolve readily in hydrocarbon solvents and are only slightly soluble in water in which they give non-conducting solutions in which the metal is clearly non-ionised. The beryllium compound of acetyl-acetone which may be taken as typical of the group is formulated:



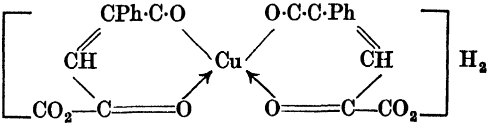
by Sidgwick, in which beryllium obtains a completed octet by co-ordinate sharing with two oxygen atoms.

Aluminium forms a similar compound with three molecules of the diketone, yielding a trichelate derivative:



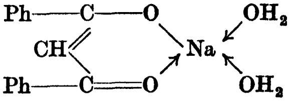
in which aluminium is hexacovalent.

In 1926, Mills and Gotts [5] prepared the co-ordination compound of bivalent copper and benzoylpyruvic acid

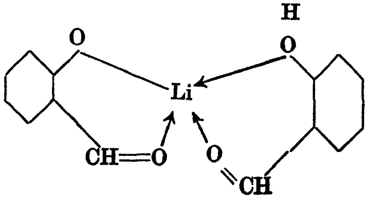


whose tetrahedral symmetry was established by its resolution into optically active isomerides. In this compound, the cupric radical which is seven electrons short of the krypton structure, receives six from the benzoylpyruvate residues, and is therefore unsaturated to the extent of one electron.

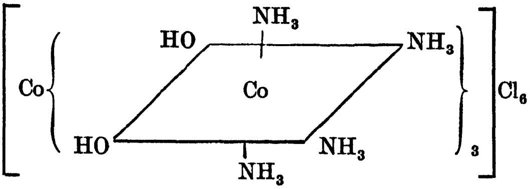
Considerable attention has been directed in recent years to the study of chelate compounds, and interesting compounds of this type have been obtained from the alkali metals. Thus sodium benzoylacetone, Ph·C(ONa) : CH·COMe, although it is a salt-like substance, insoluble in benzene, gives rise to a non-polar dihydrate [6]



in which sodium has a co-ordination number of four, while salicylaldehyde gives rise to a co-ordination compound of lithium having the structure



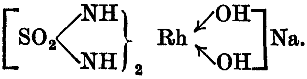
The fact that chelate compounds need not be organic in character was shown by Werner himself as far back as 1914 by resolution of the basic salt, dodecaaminohexoltetracobaltic chloride



into optically active isomerides. Recently, Mann[7] has used sulphamide to furnish an inorganic chelate group of a new type. In certain circumstances, sulphamide functions as a dibasic acid, giving rise to complex salts with rhodium and platinum:

$$[2H_2ORh(N_2H_2SO_2)_2]Na \quad \text{and} \quad [NH_3HOPt(N_2H_2SO_2)_2]Na$$

and the rhodium salt has been resolved into optically active forms, in accordance with the formula



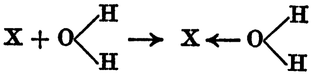
$$\left[SO_2\left<\begin{matrix}NH\\NH\end{matrix}\right\}_2 Rh\begin{matrix}\swarrow OH\\ \nwarrow OH\end{matrix}\right]Na.$$

A question of considerable interest which arises in connexion with the formation of co-ordination complexes, is the formation of additive compounds between solutes and solvents. The substances of this class which are produced from purely covalent compounds need not be discussed, but those resulting from the combination of ionised molecules and solvents are worthy of special consideration. The most familiar examples of compounds of this type are, of course, furnished by the ordinary hydrated salts of Inorganic Chemistry, but the experimental investigation of the constitution of these substances is often so difficult that it is impossible to tell whether all, or only part of the solvent molecules which appear in the empirical formula of the substance actually form part of a co-ordination complex.

Amongst the numerous compounds of this type which have been recorded in chemical literature, of which the molecular weight cannot be determined, a large number are assumed to exist from the fact that a solid phase can be produced which contains the elements in the proportion corresponding to a possible formula, which is independent within certain limits, of the actual conditions of isolation. The evidence in connexion with the salt hydrates is invariably of this type, and as we cannot determine the degree of hydration in solution, it is usually assumed that if a solid hydrate possessing a particular composition separates, this hydrate is also present as a definite molecule in the solution from which it is isolated. Similar reasoning is also applied to the compounds of ammonia of crystallisation which are obtained from solutions of salts in liquid ammonia and by treatment of salts with gaseous ammonia. There are, it must be emphasised, a number of double salts forming solid phases of definite composition, but of whose actual existence in solution, little can be said in the absence of definite experimental evidence. It is, moreover, known from X-ray measurements, that a crystal unit may contain two or more molecules which are certainly not chemically combined in any way ; the molecules being packed together in the crystal by the operation of forces which are very much more feeble than those of chemical affinity, and which are presumably due to the weak electrical fields which always surround an atom. When, for instance, the structure of the crystal is destroyed by fusion or by solution, the molecules composing the crystal unit separate. A particularly striking example of the phenomenon is furnished by solid benzene. Thus it has been shown that the crystal unit of this hydrocarbon contains two molecules of benzene, but there is no evidence whatever that there is any valency linkage between the molecules. If this can occur between similar molecules, there is all the more reason for its occurrence between dissimilar molecules, possessing appreciable polarisation, which provides a source of feeble mutual attraction.

It has also been shown that crystalline hydrates can be prepared from substances such as *methane*,[8] and even from certain of the *inert gases* ![9] Clearly then, when a substance separates from a solvent, it is possible for the crystal unit to contain solvent molecules which have no chemical connexion with the solute molecule. It is interesting to note that Werner took this question into account in his co-ordination theory of valency. Thus while he definitely assigned co-ordinate covalency linkages to certain water molecules in hydrates, he assumed that other water molecules had no part in the molecular structure of the compounds, and he furthermore supported this by showing that in such substances, some water molecules were more easily removed than others.

Since we know that salts are always ionised, even in the solid state, it must be assumed that some at least of the water molecules in salt hydrates are co-ordinated with an ion by means of the lone pair of electrons of the oxygen atom in water:



The charge on the ion is a factor of considerable importance in that the *donor*, or atom which provides the lone pair of electrons for the formation of the co-ordinate link, becomes positively polarised, while a corresponding quantity of negative electricity appears on the *acceptor* by virtue of its share in electrons which it did not previously possess. An atom will therefore tend to act as an acceptor when it is positively charged by attracting the electrons of the donor, and this is evidently the basis of the ready hydration of cations.

Sidgwick has developed a theory of anionic hydration by way of the expansion of the hydrogen duplet in water to a group of four electrons; the objections to this in the light of physical theory have already been alluded to in connexion with the polymerisation of hydrogen fluoride discussed in the previous chapter.

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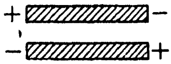
CHAPTER V

THE PHYSICAL PROPERTIES OF ELECTROVALENT, COVALENT, AND CO-ORDINATE COVALENT LINKAGES

The fundamental difference between an electrovalency and a covalency and to which reference has already been made in earlier chapters is that in the former, although the oppositely charged ions are strongly attracted to each other, there is *no real bond between them*, while in the latter, the linking orbits form part of the electronic constitution of both atoms constituting the bond. The ions in electrovalent compounds are therefore free to take up any relative positions which are convenient, while the position of the atoms of covalent compounds are definitely fixed with regard to each other in space. The ions of electrovalent compounds therefore take up a position which is determined by the forces of attraction under a given set of conditions, and only one arrangement is therefore possible and the *occurrence of stereoisomerism is thereby excluded.* Actually, the molecules of ionised compounds are not molecules in the ordinary sense of the word, but *aggregates of ions*, each keeping its electrons in the same state of binding as if it were actually isolated. Sodium chloride in the crystalline state, for instance, does not consist of molecules of the formula NaCl, but is an agglomeration of sodium and chlorine ions arranged in such a way that each sodium ion is surrounded by six chlorine ions, and each chlorine by six sodiums, in the ordinary Rock-salt structure. In covalent compounds, on the other hand, the *linkages form part of the constitution* of the atoms concerned, and it is therefore possible to have the same number of atoms or groups arranged in more than one way round a particular atom, leading to the phenomenon of *stereoisomerism.* Stereoisomerism is therefore essentially a property of homopolar or covalent linkages, and this is the reason for its occurrence *par excellence* in Carbon chemistry.

Covalency is essentially a process of *neutralisation*, and the electrical forces in a covalent compound are more or less fully satisfied within the molecule. In electrovalent compounds, on the other hand, quite another state of affairs obtains. Here, we have charged ions and the electrical disturbance in their neighbourhood is large. There are therefore strong fields of electrical force outside the molecule and a process of mutual neutralisation takes place by a sort of " head and tail " arrangement. The positive electrical field surrounding a cation in an electrovalent molecule is responsible for neutralising the bulk of the negative electricity surrounding the anion of another, and so on, which can be represented diagrammatically as follows:



The work which is therefore required to separate the molecules of ionised compounds is therefore considerably greater than that required for a similar purpose in dealing with covalent compounds.

The methods of distinguishing between electrovalent and covalent molecules depend essentially on the application of these principles, and the most obvious method is, of course, the direct observation of ionisation. The attraction between the ions in an electrovalent molecule is electrostatic and consequently when the substance is dissolved in a solvent of high dielectric constant, the ions separate and can be detected by their conductivity. Furthermore, by measuring the conductivity at different dilutions, it is possible to form an estimate of the number of ions into which the compound has dissociated. E.M.F. measurements with a reversible electrode also provide another means of determining ionic concentration, which has indeed been used with considerable success in dealing with complex ion formation in double salts. Chemical methods can also be used ; thus, the electrovalent chlorines in the co-ordination compound $[Pt(NH_3)_5Cl]Cl_3$ are distinguishable from the chlorine atom which forms part of the co-ordination complex by the fact that they are ionisable and therefore reactive to an aqueous solution of a silver salt. It is unfortunate that this direct method of distinguishing between electrovalent and covalent compounds is limited by the fact that a very large number of compounds cannot be dissolved in water without decomposition.

A proof of the existence of covalency which is still more limited is of course the occurrence of stereoisomerism, since this can only arise through true bonds between the atoms concerned. The fact that a molecule is optically active, although all the groups attached to the central atom are themselves inactive, does not necessarily imply that all the links between these groups and the central atom are covalencies, as is seen by reference to the tetrasubstituted ammonium halides, in which the four alkyl, alphyl, or aryl groups are covalently linked to nitrogen, but the halogen is present in the electrovalent form $[R_1R_2R_3R_4\overset{\oplus}{N}]\overset{\ominus}{\mathrm{Hal}}$.

When these direct methods of determining whether a link in a molecule is of an electrovalent or a covalent character cannot be applied for one reason or another, it is usually necessary to resort to less precise tests, such as that of the degree of *volatility* of the compound. Thus the characteristic of ionised molecules is the possession of much stronger external fields of electrical force than are manifested in covalent compounds, resulting in the "head and tail" process of self-neutralisation to which reference has already been made. Since the boiling-point of a substance depends on the thermal energy which is necessary to overcome the effect of molecular attraction, electrovalent substances require much more work to be done in this connexion and therefore boil at much higher temperatures than covalent compounds. In this connexion, Sidgwick quotes the somewhat striking example furnished by the behaviour of the hydrides and halides of different elements. These compounds fall into two separate classes, which are evidently dependent on the nature of the linkage between the elements concerned. Thus all the nineteen elements, one, two, three, and four places before an inert gas which are known to form hydrides, yield compounds of this type which are volatile, and in so far as they have yet been examined, do not readily conduct electricity, and may therefore be regarded as covalent. On the other hand, the alkali metals and the alkaline earths form non-volatile hydrides which are good conductors in the fused state and which liberate hydrogen at the anode; they must therefore contain the negative hydrogen ion $[\cdot H\cdot]^{\ominus}$.

A similar phenomenon is also observed with regard to the halides of the elements, which fall into two groups consisting of volatile covalent compounds and non-volatile salts. Not only do these two groups differ in the relative magnitude of the boiling-points of the substances, but what is still more interesting, they show the effect which is produced by changing one halogen for another. In covalent compounds such as the halides of silicon, the boiling-point rises as we proceed from fluorine to iodine. In ionised compounds such as the sodium salts of the four halogen acids, however, the boiling-point falls as the atomic weight of the halogen increases. The following figures which have been taken from Sidgwick's [1] book may be taken in illustration :

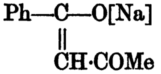
BOILING-POINT AT 760 M.M.

NaF	NaCl	NaBr	NaI
1695°	1441°	1393°	1300°
SiF_4	$SiCl_4$	$SiBr_4$	SiI_4
− 90°	57°	153°	*ca.* 290°

The figures in the case of the non-polar silicon halides are such as would be anticipated from the fact that the volatility of a normal substance decreases with increase of molecular weight. In salts, however, the boiling-point falls with increase in atomic weight, in accordance with the fact that the determining factor in these substances is the electrical attraction between the atoms, which naturally falls off as the atomic diameter of the halogen increases.

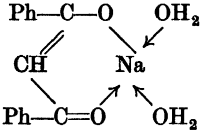
Evidence derived from the volatility of a compound is, however, by no means an infallible test between electrovalency and covalency, because of the possibility of confusion arising from polymerisation. Thus there are substances such as carborundum, CSi, in which the whole of the crystal really constitutes *one huge molecule* in which the atoms are held together by homopolar linkages. A substance of this type has no vapour pressure in the strict sense of the term since it can only melt or boil by dissociating. Since the linkages are covalencies, this requires a very high temperature and a substance such as carborundum might therefore be easily mistaken for an ionised compound, although it is actually non-polar.

Another property which is frequently of assistance in deciding between covalency and electrovalency in molecules is that of the solubility of the compound in hydrocarbon solvents of the type of petroleum and benzene. It is well known that inorganic salts are insoluble in solvents of this type, but that organic compounds usually dissolve much more readily in benzene than they do in water. An interesting illustration of this means of distinguishing between electrovalency and covalency is furnished by sodium benzoylacetone, to which reference has already been made in the previous chapter in connexion with chelation. This compound decomposes without melting on being heated, dissolves readily in water and is insoluble in benzene, in accordance with the electrovalent formula



$$\mathrm{Ph{-}\underset{\underset{\displaystyle CH\cdot COMe}{\|}}{C}{-}O[Na]}$$

On recrystallisation from dilute alcohol, however, it takes up two molecules of water, yielding what appears to be a dihydrate of the original salt. The fact that this is not mere " water of crystallisation " is, however, shown by the fact that this new substance dissolves in toluene, being evidently a co-ordinate covalent compound:



Considerable interest also attaches itself to the results of X-ray analysis of crystals in connexion with the distinction between electrovalent and covalent links. Thus it is found that ionised salts assume a *close-packed* form of the type to be expected from the fact that there is no real attachment between the cations and anions which compose the crystal lattice, other than the forces of electrostatic attraction. Covalent molecules, on the other hand, adopt an elaborate *open* structure in the crystalline state. Thus the crystal structures of beryllium oxide and calcium sulphide indicate that these molecules are covalent, whereas both the oxides of magnesium and calcium possess an ionised lattice.

The phenomenon of transition of one form of valency linkage into another is of considerable interest, and is illustrated by the case of stannic chloride. This compound is a volatile liquid, miscible with benzene, a non-conductor of electricity and, in the absence of water, shows all the characteristics of a covalent compound. In aqueous solution, however, it gives reactions for both stannic and chlorine ions, indicating that the transition from covalency to electrovalency is a facile process.

An important problem in this connexion is the extent to which compounds which are known to ionise in water are in a covalent, or electrovalent form in aqueous solution. This is actually the crux of the old problem of the behaviour of weak electrolytes of the type of acetic acid. Thus the molecular conductivity of this compound at moderate dilutions is about one per cent of that at infinite dilution, while its sodium salt resembles sodium chloride in being a strong electrolyte whose dissociation at moderate dilutions is about 80% of that at infinite dilution. The explanation is that the molecule of the sodium salt is essentially electrovalent, $[CH_3{\cdot}COO]Na$, whereas an aqueous solution of acetic acid contains an equilibrium between the covalent form, the electrovalent form, and the ions produced from the latter by dissociation:

$$CH_3{\cdot}COOH \rightleftarrows [CH_3{\cdot}COO]H \rightleftarrows [CH_3{\cdot}COO]^{\ominus} + H^{\oplus}$$

At ordinary dilutions, the equilibrium between the electrovalent form of acetic acid and the covalent form is about 99·5% in favour of the latter, and the conductivity of such a solution is therefore merely a measure of the dissociation of the remaining 0·5% of electrovalent form.

A very interesting theory of the transition of the one form of valency linkage into the other was developed by Fajans [2] in 1923 on the basis of the fact that ions are not rigid, unalterable structures, but exert a definite deforming effect on each other in the crystal lattices of electrovalent molecules. When therefore two oppositely charged ions approach each other, a certain point will be reached when the deformability which they produce on each other's electrons will cause the electrons to be diverted into *new orbits containing both atoms*, with the production of covalency linkage. The tendency towards such a transformation will of course depend on the attractive power of the cation for electrons, and upon the firmness with which the anion holds on to its electrons. The conditions will therefore be favourable to this when the *cation is small*, and when the hold of the positive nucleus on the electrons of the anion is small—that is, when *the anion is large*. A high valency or charge will furthermore tend to promote deformation, leading to the transformation of electrovalency into covalency. Opposite conditions, namely, a large cation and small anion and low charge will favour the production of polar compounds, and the general truth of Fajan's theory can be seen by reference to the Periodic Table, although there are a number of exceptions to these rules.

The problem of transition from covalent to electrovalent linkage is treated on somewhat different lines by Samuel on the basis of a molecular picture in which electrovalency constitutes merely an extreme case of covalency. In the former, the electron of the positive partner is of course completely transferred to the negative atom, in which it proceeds to fill one of the "electronic gaps" which serve to distinguish this element from the next inert gas in the period concerned. Samuel and Lorenz[3] visualise a somewhat similar process in the formation of a normal covalency A—B, in that they assume that an electron is partly transferred from the first atom A to the second in such a manner that it counts towards the electronic configuration of B, but is still partly under the influence of the electrical field of A, which thereby acquires a certain degree of positive polarity. This may be translated into wave-mechanical quantum terms by saying that in electrovalency the electron of the positive partner joins the same quantum group as an electron of the negative partner, whereas in covalency these electrons form a similar quantised group in the configuration of the molecule. This theory which has much to recommend it from certain points of view, implies that in the formation of a covalency one atom necessarily acquires a certain degree of positive polarity, while a corresponding degree of negative polarity appears on the second atom, and recognises therefore only *one* form of chemical linkage, the extreme of which is furnished by electrovalency in which the first atom completely relinquishes its hold on one of its electrons. It necessitates abandoning the Octet Rule for the following postulate: The "negative" partner in a molecule always adds to its electronic configuration (completely in electrovalency and only partly in covalency) the electrons required to obtain the number present in the next inert gas, whereas the "positive" partner loses partly or completely the number of electrons which will leave it a residue possessing the electronic configuration of the inert gas which precedes it in the Periodic System. By this means, difficulties such as those presented by the existence of compounds such as sulphur hexafluoride and osmium octafluoride disappear, since elements of this type are assumed to exhibit hexacovalency and octacovalency on account of the fact that they possess six and eight valency electrons, respectively.

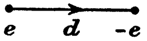
On the basis of this theory it will be seen that the question as to whether a molecule will be covalent or electrovalent depends on the energy with which the "positive" partner resists the loss of the electron concerned and the electronic affinity of the "negative" partner. Where the first of these is high and the second is low, typical covalency will be manifested, but when the force of attraction of the " negative " partner for the electron of the " positive " partner approaches in magnitude the attraction of the latter for this, a comparatively small amount of additional energy such as that provided by a solvent of high dielectric constant will be sufficient to carry covalency over to electrovalency. Thus hydrogen chloride, which is covalent both in the gaseous and liquid state becomes electrovalent when dissolved in water. Similarly, silver chloride, which is definitely covalent in the vapour state and gives rise to a definite band spectrum, is known to be dissociated into silver ions and chlorine ions in the fused condition.

With regard to the properties of the co-ordinate link or semipolar double bond, the first point which must be emphasised is that a co-ordinate link is in general more easily ruptured than a normal covalency. The characteristic, indeed, of a large number of co-ordination compounds is that they are formed from the combination of atoms which previously belonged to more-or-less saturated molecules, and the complex can therefore be broken down by a retrograde reaction involving comparatively little energy. A covalency, however, cannot behave in this way since its rupture gives rise to unsaturated univalent radicals of high energy content, which are as a consequence very unstable.

Secondly, since a co-ordinate covalency is produced by a process of unequal sharing corresponding to a process of *intramolecular ionisation*, its production involves the generation of comparatively powerful electrical disturbances which are manifested in the production of a high dielectric constant in the compound. Furthermore, the co-ordinate link occupies a position which is intermediate between normal covalency and electrovalency with regard to volatility, as might of course be anticipated from the presence of the powerful electrical disturbances consequent on unequal sharing.

There are two main methods of establishing the presence of semipolar double bonds in molecules, the first of which involves direct measurement of the *polarisation*, that is, the extent to which there are definite localisations of positive and negative electricity in the molecule, and the second of which is the determination of Sugden's parachor, which is separately treated in the following chapter.

The polarisation in a molecule follows from its molecular electrical moment, which can be calculated from the measurement of its dielectric constant by Debye's method, to which brief reference may be made. It was emphasised by Lewis that the characteristic of an electrovalent molecule is the possession of an *electrical dipole moment* μ, which is equal to the product of the charge e on either of the ions concerned and the distance, d, between the atomic centres:

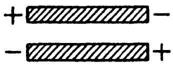


A covalent molecule will have a zero dipole moment if its electrons are symmetrically arranged round the nuclei—that is *if the electrical centre of gravity of the electrons coincides with the electrical centroid of the nuclei.* Any distortion from this such that the mean electrical centre of all the electrons and the corresponding centre of all the positive nuclei do not coincide, will be equivalent to an electrical dipole giving rise to a definite electric moment. In the presence of an electrical field, such molecules will tend to orient themselves in the direction of the field, just as magnets do in a magnetic field. This tendency will be opposed by thermal agitation, with the result that a statistical average degree of alignment will take place, depending on the temperature. The molecular fields thus reinforce the original exciting electrical field, but, in addition to this, the electrical moments of the oriented molecules will be augmented owing to a further separation of positive and negative electricity.

The dielectric constant ε which depends essentially on the gross change in the strength of electrical field due to the presence of the molecules can be divided into two terms, the first of which may be termed the *orientation polarisation* P_μ and represents the contribution of the dipoles, and the second of which $P_A + P_E$ represents the *distortion* effect. The latter can be divided into two parts, P_A *the atom polarisation*, and the *electron polarisation* P_E. The electron polarisation is the only part which contributes to the dielectric constant in the rapidly oscillating electrical fields of visible light. The atom polarisation term P_A can in fact only be determined if the necessary optical data for the far infra-red region are known. Its importance is just as fundamental as that of the dipole moment, however, because it provides a measure of the tendency towards incipient dissociation into ions.

We can therefore write: $P = P_\mu + P_E + P_A$, and it is of course the first term P_μ which is a measure of the dipole moment of the undistorted molecule concerned, and in practice it is necessary to distinguish between this and the distortion effect due to the further intramolecular ionisation produced by the exciting field. Since no orientation is possible in the solid condition, the dielectric constant in this state gives a measure of the distortion effect, and subtraction of this from the moment observed in the liquid state will give a measure of the effect of the molecular dipole. Another method, which is also of considerable value, is to use a rapidly alternating current as the exciting force, such that the molecules have not sufficient time to orientate themselves and a lower value for the dielectric constant is obtained, which when compared with the result obtained in the ordinary way, indicates the magnitude of the distortion effect.

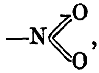
These considerations all apply primarily to vapours, but give satisfactory results in dealing with measurements on dilute solutions of compounds in inert solvents such as benzene. The results obtained in dipole moment determination in the cases of strong solutions and liquids are not nearly so satisfactory owing to the "self-neutralisation" effect of dipole association of the type:



In a molecule such as ethane, the electrons of the carbon to carbon bond are symmetrically distributed, and the substance has therefore a zero dipole moment. If, however, we replace one of the carbon atoms by another atom, possessing the same number of electrons in the combined state but a higher positive nuclear charge, such as nitrogen, or oxygen, the electrical symmetry will be disturbed owing to the difference between the nuclear charges which control the electrons in the covalency (C, 6; N, 7; O, 8). This results in the production of a dipole, which can be estimated by measurement of the dielectric constant of methylamine and methyl alcohol:

H_3C——CH_3	H_3C——NH_2	H_3C——OH
$\mu = 0 \times 10^{-18}$ e.s.u.	$\mu = 1{\cdot}3 \times 10^{-18}$ e.s.u.	$\mu = 1{\cdot}67 \times 10^{-18}$ e.s.u.

With methyl fluoride, the disparity between the atomic numbers of the atoms forming the covalency is still greater, with the production of a dipole moment of $1{\cdot}8 \times 10^{-18}$ e.s.u. These dipole moments produced in this way are of a type similar to, but of course of much smaller magnitude than those encountered in electrovalent molecules.

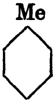
A semipolar double bond such as that between the nitrogen and oxygen atoms composing the nitro group  $-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$, therefore results in a well-defined state of polarisation, and it has been shown from measurements of the dielectric constants of simple nitrohydrocarbons that their molecules always possess a dipole moment of the order of $3{\cdot}8 \times 10^{-18}$ e.s.u. It may, however, be noted that this is somewhat smaller than that calculated from the accepted value of the sum of the atomic radii of the elements concerned (1·3AU) and the electronic charge ($4{\cdot}77 \times 10^{-10}$ e.s.u.), which is $6{\cdot}2 \times 10^{-18}$ e.s.u., suggesting that the electrons of the semipolar double bond are drawn towards the positive end with a consequent shrinkage in the measurable electrical moment.

A point of considerable interest in connexion with the polarisation of molecules is the effect of increasing the length of carbon chains in homologous series. Thus the dipole moment of methyl alcohol is, as has already been indicated, $1{\cdot}67 \times 10^{-18}$ e.s.u., but the effect of increasing the length of the carbon chain on this is to all intents and purposes negligible, as will be seen from the following figures for the dipole moments of alcohols up to *n*-amyl:

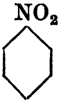
Alcohol	*Dipole Moment*
EtOH	$1{\cdot}72 \times 10^{-18}$ e.s.u.
n-$C_3H_7{\cdot}OH$	1·65 × „ „
n-$C_4H_9{\cdot}OH$	1·74 × „ „
n-$C_5H_{11}{\cdot}OH$	1·66 × „ „

This indicates clearly that the dipole moment for these compounds is essentially a function of the carbon-hydroxyl linkage, and that the remaining part of the molecule has little or no effect on polarisation.

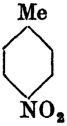
Particular interest attaches itself to the dipole moments of substituted-benzene derivatives from the point of view of the electronic theory of aromatic substitution developed in Chapter VIII. In considering these, it must be remembered that the dipole moments of aromatic compounds have definite *direction* in the sense that the polarisation of a nuclear methyl group, for instance, is opposite to that of the polarisation produced by a nitro group. Thus, toluene for instance has a dipole moment of $0{\cdot}4 \times 10^{-18}$, and nitrobenzene has a dipole moment of 3·9 × 10^{-18} e.s.u., but the moment of *p*-nitrotoluene is 4·5 × 10^{-18} e.s.u., showing that the moments are of opposite sign since if they were both directed towards the aromatic nucleus, the resultant dipole moment would be of the order of the *difference* between them, that is 3·5 × 10^{-18} e.s.u.



0·4 × 10^{-18} e.s.u.

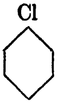


3·9 × 10^{-18} e.s.u.

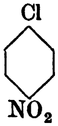


4·5 × 10^{-18} e.s.u.

The moment of chlorobenzene, on the other hand, is 1·5 × 10^{-18} e.s.u., and that of *p*-nitrochlorobenzene 2·6 × 10^{-18} e.s.u., showing that in this case the dipole moment of chlorine is in the same direction as that of the nitro group.



1·5 × 10^{-18} e.s.u.

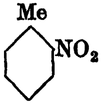


2·6 × 10^{-18} e.s.u.

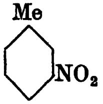
On the basis of relations of this type, it is therefore possible to assign algebraic signs to the dipole moments of substituents attached to an aromatic nucleus, on the lines first suggested by Højendahl, and a few of these have been collected in the table given hereunder.

Substituent	*Dipole Moment*
NO_2	— 3·9 × 10^{-18} e.s.u.
OH	— 1·7 ,, ,,
Cl	— 1·5 ,, ,,
Br	— 1·5 ,, ,,
I	— 1·25 ,, ,,
CO_2H	— 0·9 ,, ,,
Me	0·4 ,, ,,
NH_2	1·5 ,, ,,

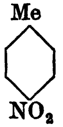
If the dipole moments of the nitrotoluenes are examined, it will be seen that the polarisation of the nitro and methyl groups act in opposite directions:



$3{\cdot}75 \times 10^{-18}$ o.s.u.



$4{\cdot}2 \times 10^{-18}$ e.s.u.



$4{\cdot}5 \times 10^{-18}$ e.s.u.

It was first pointed out by Sir J. J. Thomson [3] some ten years ago, that in compounds containing two substituents creating dipoles in an aromatic nucleus, that the moment of the molecule as a whole should be given by the vectorial addition of the moments of the individual dipoles. If m_1 and m_2 are the dipole moments of the two substituents in an aromatic nucleus, and θ is the angle of inclination between these, then the dipole moment of the compound is given by the vector sum of the two dipoles, that is by

$$\mu = \sqrt{m_1^2 + m_2^2 + 2m_1m_2 \cos\theta}$$

If, as there appears to be very good reason to suppose, the aromatic nucleus is indeed flat, then the angle between the dipoles in an *ortho*-disubstituted derivative may be assumed to be 60°, that between the dipole of a *meta* compound 120°, and 180° in the case of a *para* isomer. On the basis of this, it is possible to calculate the dipole moments of disubstituted derivations of benzene from data obtained from monosubstituted derivatives. The agreement between such calculation and the observed dipoles obtained for certain disubstituted benzene derivatives is indicated in the table given hereunder.

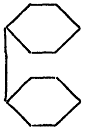
Compound.	μ *observed.*	μ *calculated.*
o-Dinitrobenzene . .	5·95	$6{\cdot}50 \times 10^{-18}$ e.s.u.
m-Dinitrobenzene . .	4·02	3·75 ,, ,,
o-Nitrotoluene . .	3·56	3·62 ,, ,,
p-Nitrotoluene . .	4·30	4·18 ,, ,,
o-Chloronitrobenzene .	4·25	4·75 ,, ,,
m-Chloronitrobenzene .	3·38	3·27 ,, ,,
p-Chloronitrobenzene .	2·52	2·17 ,, ,,
o-Dichlorobenzene . .	2·25	2·68 ,, ,,
m-Dichlorobenzene . .	1·48	1·55 ,, ,,
p-Dichlorobenzene . .	0	0 ,, ,,

When the two substituents are identical and in the *para* position, self-neutralisation naturally takes place, with the result that compounds such as *p*-dichlorobenzene and *p*-dinitrobenzene, for instance, have zero dipole moments. There are, however, certain exceptions to this. Thus di-*p*-ethoxybenzene which would be expected to have a zero dipole, actually has been shown to possess a dipole moment of $1{\cdot}7 \times 10^{-18}$ e.s.u., and other similar abnormalities have been observed in the case of compounds having —O·X and —NR_2 groups attached to a benzene ring. The probable explanation of this is that when a substituent is attached to a benzene ring by means of oxygen or nitrogen, the dipole vector does not operate in the *same plane* as the aromatic nucleus. The moment of the ethoxyl group attached to a benzene ring is regarded, for instance, as being compounded of two separate moments, the one due to C_6H_4—O acting in the plane of the aromatic nucleus, and the other due to O—Et acting in a plane inclined at 110° to the plane of the nucleus.

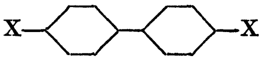
A most interesting application of the use of the dipole moment in elucidating constituted problems is provided by the recent work of Sidgwick and his collaborators on the structure of the *iso*cyanide group and carbon monoxide.[4] It was found that *p*-tolyl-*iso*cyanide has a dipole moment of $4{\cdot}0 \times 10^{-18}$ e.s.u., while the dipole moment of *p*-chlorophenyl*iso*cyanide is $2{\cdot}07 \times 10^{-18}$ e.s.u. This indicates therefore that the dipole moment of the *iso*cyanide group attached to the benzene nucleus is approximately $3{\cdot}6 \times 10^{-18}$ e.s.u., but it will be observed that this implies that the carbon atom of the isocyanide radical is the negative end of the dipole, or using Sidgwick's nomenclature : $> \mathrm{CN}\underset{=}{\rightarrow}\mathrm{C} = 3{\cdot}6 \times 10^{-18}$ e.s.u. The structure of the *iso*cyanide group must therefore involve a semipolar double bond—$\overset{+}{\mathrm{N}}\underset{=}{\rightarrow}\overset{-}{\mathrm{C}}$, and this receives further confirmation from the measurement of the parachor of certain *iso*cyanide derivatives. The carbon atom of the *iso*cyanide group is not therefore divalent as suggested by the older formulæ for compounds of this class, and one very interesting conclusion which follows from this picture of the isocyanide radical is that the ions derived from the tautomeric forms of hydrocyanic acid are identical $[\mathrm{N} \equiv \mathrm{C}]^{\ominus}$, and this is the reason for the well-known conflicting evidence with regard to the chemical behaviour of this acid and its salts.

In a similar manner, it has been shown that carbon monoxide probably has the structure $\mathrm{C}\underset{=}{\leftarrow}\mathrm{O}$, since the small dipole of this compound ($0{\cdot}12 \times 10^{-18}$ e.s.u.) suggests a transference of oxygen electrons to the carbon atom to neutralise the large polarisation which would be associated with the structure $C{=}O$.*

Amongst the other applications of the measurement of the dipole moment to chemical problems, reference may be made to the problem of the structure of diphenyl. Thus the Kaufler formula for diphenyl

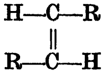


in which one ring is supposed to be folded over the other has been discounted by dipole measurements as well as by other experiments. The p-p^1-di-derivatives,



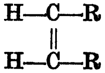
have a dipole moment of zero, whereas if the Kaufler formula was correct the two p-p-groups should act in the same sense and not neutralise each other, and the compound should possess a moment dependent partly on the angle of inclination of the two rings.[5]

The dipole moment has also proved of service in connexion with stereochemical problems. Thus in the case of *cis-trans* isomerism in disubstituted ethylene, the *trans* isomeride



$$\begin{array}{c} H{-}C{-}R \\ \| \\ R{-}C{-}H \end{array}$$

would be expected to be non-polar in character, while the *cis* isomer



$$\begin{array}{c} H{-}C{-}R \\ \| \\ H{-}C{-}R \end{array}$$

would be expected to have a definite dipole moment. Actually, it has been shown by Errera[6] that in the case of the dichloro, and dibromo derivatives of ethylene of this type that the *trans*-forms are non-polar, while the *cis*-isomerides exhibit moments of the order of about $1{\cdot}5 \times 10^{-18}$ e.s.u. Similarly, measurement of the dipole moment of oximes has also been used as a means of deciding between the opposed theories of Hantzsch and Meisenheimer with regard to the *syn*- and *anti*- configurations of the *N*- ethers of *p*-nitrobenziphenoneoxime:

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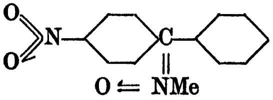
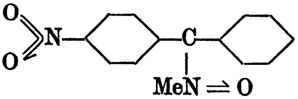
* The energy of adiabatical dissociation of carbon dioxide, deduced from Abel and Dennison's recent analysis of its infra-red spectrum (*Phys. Rev.*, 1933, **44**, 99), is in numerical agreement, however, with the view that there are only two linkages between carbon and oxygen in carbon monoxide (Lessheim and Samuel, *Current Sc.*, 1934, **2**, 347).



Syn



Anti

Thus the $-\mathrm{N} \rightleftharpoons \mathrm{O}$ group should have a moment of the order of the nitro group, and the dipole moment of the *syn* compound should therefore be large and that of the *anti* compound small. It has been found by Sutton and Taylor [7] that the compound to which Meisenheimer has assigned the *syn*-formula has a moment of $6{\cdot}6 \times 10^{-18}$ e.s.u., while that of the isomer to which he has assigned the *anti* structure has a moment of only $1{\cdot}09 \times 10^{-18}$ e.s.u. This therefore appears to furnish conclusive evidence in favour of Meisenheimer's theory.

At this stage, it appears desirable to say something with regard to the Raman Effect, since Raman data, when fully interpreted, promise to provide one of the most accurate means of obtaining structural knowledge of molecules.

It was observed by Sir C. V. Raman [8] in the course of an investigation on the scattering of light by certain carefully purified liquids that light of frequencies different from that of the incident light appeared in the scattered radiation, and that these frequency differences were characteristic of the liquid under examination. When the incident light was of monochromatic character, it was found that the scattered light was of a spectral nature consisting in some cases of lines, and in others of more or less diffuse bands. This alteration in frequency has been termed the *Raman effect*, and can be observed with solids as well as with solutions of different compounds, and the explanation which is given of the phenomena may be represented as follows:

$$\underset{\text{(normal)}}{\text{Molecule}} + \text{Radiation} \rightleftharpoons \underset{\text{(excited)}}{\text{Molecule}} + \underset{\substack{\text{(altered}\\\text{frequency)}}}{\text{Radiation}}$$

If v_1 and v_2 represent the frequencies of the incident and the scattered light respectively, the energy associated with the incident and scattered rays will on quantum principles, be hv_1 and hv_2, and the difference between these will correspond to the energy which has been transferred to the molecules of the liquid under examination. That is, $h\ (\nu_1 - \nu_2)$, and the frequency of the oscillations absorbing this radiation which is termed the *Raman frequency* will be the difference between ν_1 and ν_2. These frequency differences between exciting and scattered lines correspond to changes in one of the characteristic vibrational or rotational levels of the molecule. It has been shown that rotational transitions are indicated by lines very near the spectral line scattered without frequency change, and vibrational disturbances are associated with lines much farther away from this.

It has been possible to identify lines of particular frequencies with the vibration of certain chemical bonds in the molecule, and it is to this that the Raman spectra of compounds owe their present importance. Thus, the C—H linkage contained in aliphatic compounds produces a line in the spectrum of the scattered light with a frequency displacement of about 2930 cm^{-1}, corresponding to a wave-length of 3·41 μ. The C—H bond is, however, different in benzene derivatives, in which it gives rise to a frequency difference of 3050 cm^{-1}. Both of these values are in excellent agreement with the values for these wave-lengths deduced from the position of the absorption maxima in the infra-red ascribed to the oscillation of this linkage in aliphatic and aromatic compounds. Substances such as toluene, which contain both the aromatic and the aliphatic forms of the C—H link give rise to lines corresponding to both types in their Raman spectra.

Amongst the applications of the Raman effect to structural problems, reference may be made to the confirmation of the structure assigned to the *iso*cyanide group on the basis of dipole moment measurements. Thus the characteristic Raman lines of *iso*cyanide derivatives indicate that a triple linking must be present between carbon and nitrogen, which is evidently the co-ordinate structure $\mathrm{C}\overset{\leftarrow}{=}\mathrm{N}$.

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CHAPTER VI

THE PARACHOR AND ITS APPLICATIONS

The new physical constant discovered by Sugden[1] in 1924 in connexion with the relation between surface tension and density, and which he has named the *parachor*, has proved one of the most valuable means of distinguishing between normal covalency and co-ordinate covalency linkages in molecules.

As has already been pointed out, electrovalencies tend towards the production of smaller volumes than covalencies, and an effect intermediate between the two is to be anticipated in the case of the co-ordinate link. That is to say, that a semipolar double bond would be expected to give rise to a closer-packed structure than a normal covalency. This effect could not, however, be observed without some means of determining molecular volume by methods considerably more accurate than those which form the basis of the classical researches of Kopp and Traube, and other early investigators. Sugden has pointed out, that for the accurate determination of molecular volume, it is necessary to make allowance for the effect of the very large internal pressures of liquid manifested in surface tension phenomena, and his parachor determination is essentially an accurate molecular volume determination in which due regard is paid to this important factor.

It was discovered by McLeod in 1923, that the relation between surface tension and density was given by the expression:

$$\frac{\gamma^{\frac{1}{4}}}{D - d} = \text{a constant},$$

where D and d are the densities of the liquid and vapour phases respectively, and γ is the surface tension at the same temperature. Now suppose that D_1 and d_1 are the densities of liquid and vapour when the surface tension has an arbitrary value γ_1, we can then write

$$C^{\frac{1}{4}} = \frac{\gamma^{\frac{1}{4}}}{D - d} = \frac{\gamma_1^{\frac{1}{4}}}{D_1 - d_1}$$

where γ, D, and d are the surface tension, density of liquid, and density of vapour at any temperature.

Hence

$$D_1 - d_1 = (D - d)\frac{\gamma_1^{\frac{1}{4}}}{\gamma^{\frac{1}{4}}}.$$

If the standard surface tension γ_1, is suitably chosen, then d_1 is very small in comparison with D_1 and may be neglected, and we can write

$$D_1 = (D - d)\frac{\gamma_1^{\frac{1}{4}}}{\gamma^{\frac{1}{4}}}.$$

If we now invert this equation and multiply both sides by the molecular weight M of the substance under investigation, we obtain the expression

$$\frac{M}{D_1} = \frac{1}{\gamma_1^{\frac{1}{4}}}\cdot\frac{M\gamma^{\frac{1}{4}}}{D - d}$$

which is the molecular volume at this surface tension. This is equal to $\frac{MC^{\frac{1}{4}}}{\gamma_1^{\frac{1}{4}}}$ and is therefore proportional to the fourth root of McLeod's constant, multiplied by the molecular weight. The magnitude of $\gamma^{\frac{1}{4}}$ merely affects the proportionality factor $\frac{1}{\gamma_1^{\frac{1}{4}}}$, and Sugden therefore takes it as unity, giving the equation:

$$[P] = \frac{M\gamma^{\frac{1}{4}}}{D - d} = M\cdot C^{\frac{1}{4}}$$

where [P] is the *parachor*.

It has been shown by Sugden and his collaborators [2] that the values of this new constant show the same kind of additive and constitutive relations as the uncorrected molecular volumes, the value being expressible as the sum of a series of terms for the constituent atoms, together with others for particular forms of linkage. The double bond, semipolar double bond, closed rings, and so on, have characteristic constants which have been experimentally determined with highly purified specimens of suitable compounds. The agreement is, of course, much closer than in the old measurements on molecular volume, and the old difficulty with regard to the selection of comparable temperatures is eliminated since the parachor is independent of temperature.

The table given hereunder shows the values for some of the commoner elements and also for the structural constants:

C = 4·8
H = 17·1
N = 12·5
P = 37·7
O = 20·0
S = 48·2
F = 25·7
Cl = 54·3
Br = 68·0
I = 91·0

Triple Bond = 46·6
Double Bond = 23·2
Three-membered ring = 16·7
Four-membered ring = 11·6
Five-membered ring = 8·5
Six-membered ring = 6·1

The application of the parachor may be illustrated by the case of chloroform:

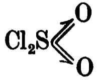
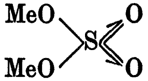
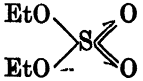
1 Carbon Atom = 4·8
1 Hydrogen Atom = 17·1
3 Chlorine Atoms = 162·9

Parachor = 184·8

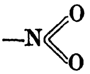
Actually the observed value for chloroform is 183·2.

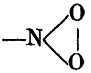
Sugden's theory has been tested with well over two hundred liquids and the calculated values give an agreement of the order of one per cent with the results of experiment.

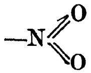
When Sugden examined co-ordinate compounds, he observed that whereas an ordinary double bond gives an increase of 23·2 units in parachor, a semipolar double bond produces a small *decrease* in parachor, averaging − 1·6 units, due to the electrostatic attraction between the poles. The figures for some of the compounds examined in this connexion are given in the following table.

Compound	[*P*] *Observed*	*Σ P Calculated*	*Semipolar Double Bond*
$Cl_3P \rightleftharpoons O$	217·6	220·6	− 3·0
$(PhO)_3P \rightleftharpoons O$	686·5	687·7	− 1·2
$Cl_2S \rightleftharpoons O$	174·5	176·8	− 2·3
	193·3	196·8	− 1·65 × 2
	238·9	240·4	− 0·75 × 2
	313·8	318·4	− 2·3 × 2

Particular interest attaches itself to the nitro group; the calculated values of the parachor for the formulæ (I), (II), and (III) being 98·9, 69·2, and 74·1 respectively.

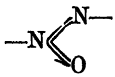

(I)

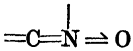

(II)


(III)

We know, of course, from the evidence discussed in the previous chapter that only the third formula is possible, but the parachor provides an interesting confirmation of this in that the average value obtained from thirteen different compounds containing the nitro group is 73·0.

In a similar manner, the parachor for azoxybenzene and the N-methyl ether of benzaldoxime indicates that these compounds contain a semipolar double bond between nitrogen and oxygen:




$=C=\overset{|}{N}\Rightarrow O$

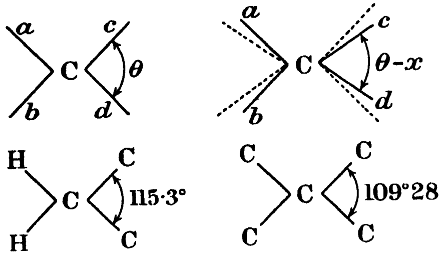
Compound	[*P*] *Observed*	[*P*] *Calculated* (for one semipolar double bond)
Azoxybenzene . . .	444·7	446·6
N-Methyl ether of benzaldoxime . . .	325·9	321·1

On the other hand, the parachors of nitrosyl chloride and of the esters of nitrous acid indicate that these compounds do not contain a co-ordinate link, and possess formulæ of the type X—N=O. Similarly, it has been shown that the isothiocyano radical in thiocarbimides is non-polar.

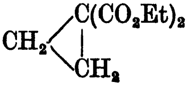
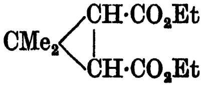
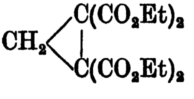
Compound	[*P*] *Observed*	[*P*] *Calculated*
Nitrosyl Chloride . .	108·1	110·0
n-Butyl Nitrite . .	251·8	248·8
Allylthiocarbimide . .	232·4	235·0

The parachor has also proved of considerable assistance in dealing with a number of structural problems of Organic Chemistry, and in this connexion it is interesting to note that the parachor calculated for benzene on the basis of the Kekulé formula (207·1) agrees within 0·5% with the observed value of 206·2.

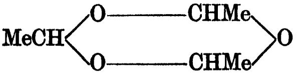
An interesting application of the parachor has been made by Sugden in connexion with the Modified Strain Theory of Thorpe and Ingold,[3] to which reference may be made at this point. As is well known, the basis of this theory is that the pushing apart of two of the valencies (*a* and *b*) of a tetrahedral carbon atom causes the remaining pair (*c* and *d*) to approach each other; the original angle between the latter pair being deflected from a value θ to a new value $\theta - x$. Ingold's stereochemical calculations on the basis of the atomic volumes of carbon and hydrogen, indicate that the angle between the carbon to carbon valencies of a polymethylene unit is quite appreciably larger than the corresponding angle of a tetrahedral carbon atom in which all four valencies are attached to carbon, *viz.*



The effect of a *gem*-complex RR, is therefore to decrease the angle between the carbon to carbon valencies of a polymethylene grouping which have to approach one another to permit ring formation, and this is the explanation of their capacity for promoting ring formation, and stabilising highly strained rings of the *cyclo*propane type. It will be seen, however, that this effect of a *gem*-complex corresponds to a decrease in unsaturation, which should be accompanied by a small decrease in parachor. That this is actually the case is shown by the parachors of ethyl *cyclo*propane-1 : 1-dicarboxylic acid, ethyl caronate, and ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate, all of which show a definite decrease in parachor.

	[*P*] *Observed*	[*P*] *Calculated*	*Decrease*
 $CH_2<\begin{array}{l}C(CO_2Et)_2\\ \mid\\ CH_2\end{array}$	417·1	419·3	− 2·2
 $CMe_2<\begin{array}{l}CH\cdot CO_2Et\\ \mid\\ CH\cdot CO_2Et\end{array}$	493·2	496·3	− 3·1
 $CH_2<\begin{array}{l}C(CO_2Et)_2\\ \mid\\ C(CO_2Et)_2\end{array}$	701·1	704·9	− 3·8

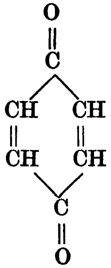
A number of similar applications have also been made by Sugden to structural problems. Thus the parachor determination of paraldehyde ([P] obs. = 298·7) supports the six-membered ring formula

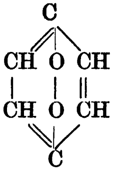


([P] calc. = 300·1)

It has also been shown that *p*-benzoquinone[4] has the ordinary diketone formula (IV), and not the peroxide structure (V) suggested by Graebe,[5] Hartley[6] and others.

(IV)





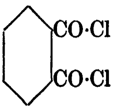
(V)

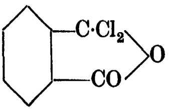
[P] calc. = 236·1 [P] calc. = 219·0

[P] observed = 236·8.

Similarly, the parachors of the isomeric forms of phthalyl chloride (m.p. 15° and 88·5° respectively) indicate that the more easily fusible form has the symmetrical structure (VI), while the higher melting and less stable form has the unsymmetrical structure (VII) in accordance with the view of Ott and Pfeiffer.[7]

(VI)

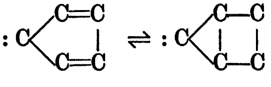




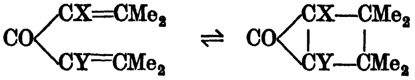
(VII)

[P] calc. = 377·5 [P] calc. = 362·8
[P] obs. = 373·9 [P] obs. = 367·8

A particularly interesting application of the parachor has also been made in connexion with the mobile phorone derivatives studied by Ingold and Shoppee,[8] to which brief reference may be made. The five-carbon intra-annular change discovered by Farmer, Ingold, and Thorpe in 1922:[9]



implies the possibility of a similar change between double bonds situated in open-chain olefinic compounds, resulting in a type of ring-chain tautomerism, independent of mobile hydrogen. This was verified for certain phorone derivatives (VIII ⇌ IX) by Ingold and Shoppee in 1928.

(VIII)

(IX)

Phorone (X=Y=H) itself is undoubtedly of the open-chain type (VIII), being a bright yellow, highly refractive substance with a parachor ([P] = 367·9) which is almost normal ([P] calculated for the open-chain structure VIII = 372·2).[10] The change to the isomeric cyclic structure (IX), however, produces a decrease in unsaturation which is shown in the parachor. Thus the dichloro derivative (X=Y=Cl) has a parachor of 427·7, whereas the calculated value for the open-chain structure (VIII) is 446·6. This anomaly (– 18·9) will be seen to be close to that calculated for cyclisation, which is – 21·4. The dibromo derivative (X=Y=Br), however, gives a parachor of 463·2 (Calculated P for open-chain structure = 474·0), indicating the presence of a more balanced equilibrium of tautomers than in the case of the dichlorophorone.

Considerable interest attaches itself to the parachor in connexion with the theory of the singlet linkage in that the determination of the parachors of compounds of the type of phosphorus pentachloride and antimony pentachloride provides evidence in support of the contention that the labile halogen atoms in these substances are held by semipolar single bonds, which is fully discussed in the following chapter.

References

1. Sugden, *J. Chem. Soc.*, **125**, 1185, 1924.
2. Sugden, Reed, and Wilkins, *J. Chem. Soc.*, **127**, 1525, 1925; Sugden and Whittaker, *ibid.*, p. 1868; Sugden and Wilkins, *ibid.*, p. 2517.
3. Ingold, *J. Chem. Soc.*, **119**, 305, 1921.
4. Garner and Sugden, *J. Chem. Soc.*, 1927, p. 2877.
5. Graebe, *Annalen*, **146**, 16, 1868.
6. Hartley and Leonard, *J. Chem. Soc.*, **95**, 34, 1909.
7. Ott and Pfeiffer, *Ber.*, **55**, 413, 1922.
8. Ingold and Shoppee, *J. Chem. Soc.*, 1928, p. 365.
9. Farmer, Ingold, and Thorpe, *J. Chem. Soc.*, **121**, 128, 1922.
10. Sugden, *J. Chem. Soc.*, 1928, p. 410.

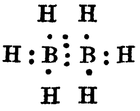
CHAPTER VII

THE THEORY OF SINGLET LINKAGES

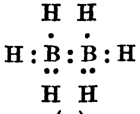
As has been indicated in previous chapters, the study of the ordinary non-ionised compounds leads to the view that a covalency is composed of two electrons, and London's theory of covalency is indeed essentially a process of coupling by means of resonance, the spins of two electrons belonging to the atoms which combine to form a homopolar molecule. The occurrence of the hydrogen molecule ion $\overset{\oplus}{[H_2]}$, whose average life is very long in comparison with the lives of the ordinary excited atoms found in positive ray discharge tubes, indicates clearly that the duplet rule is by no means infallible, since this ion can contain only *one electron.*

The wave mechanical aspect of $\overset{\oplus}{[H_2]}$ has been worked out by Burrau,[1] and its formation can be visualised as due to the bringing up of a second proton to an ordinary hydrogen atom in which the electron is rotating round the positive nucleus, which Heisenberg [2] and Dirac [3] have shown, will result in the oscillation of the electron between the orbits of both positive nuclei. From the wave mechanical equations it is possible to calculate the region surrounding the nuclei in which the electron may be found, and when the interchange of energy is such as to render possible the existence of a stable molecule containing a non-polar bond, the electron will lie in the region between the two positive nuclei such that it is *shared* between them. The single electron linkage, or as it is most commonly termed " the singlet," therefore corresponds largely to a somewhat labile form of covalency linkage.

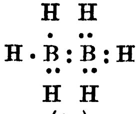
The careful investigations of Stock and his pupils on the boron hydrides have established the existence of diborane B_2H_6, in which there are clearly seven links. Now apart from the two K electrons of boron, there are twelve available electrons—six from the hydrogen atoms and three from each of the boron atoms. It is therefore impossible to formulate the compound without assuming that at least two hydrogen atoms are attached to boron by singlet linkages, and in accordance with the state of " incipient dissociation " implied by such formulation, the compound is known to be unstable and to act as a very powerful reducing agent. There are clearly three possibilities, (I), (II), and (III). In the first of these, four hydrogen atoms are held by singlets to the boron atoms, both of which are thus enabled to complete their octets. In (II) and (III), only two hydrogen atoms are held by singlets, but the formula (III) appears highly improbable on account of its unsymmetrical character.


$H:\underset{H}{\overset{H}{B}}\vdots\underset{H}{\overset{H}{B}}:H$

(I)


$H:\underset{H}{\overset{H}{B}}:\underset{H}{\overset{H}{B}}:H$

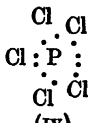
(II)


$H\cdot\underset{H}{\overset{H}{B}}:\underset{H}{\overset{H}{B}}:H$

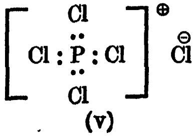
(III)

The hydrogen molecule ion $[H_2]^{\oplus}$ and diborane therefore represent cases in which the electronic structures of the molecules cannot be represented by any other means than those involving singlet linkages, but there are reasons for believing that the manifestation of singlet linkages is by no means confined to these two examples, and a particularly interesting case is furnished by the much-debated structure of phosphorus pentachloride.

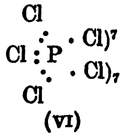
Three formulæ, (IV), (V) and (VI), have at different times been suggested for this compound. The first of these, (IV), assumes that the octet rule is abandoned in this compound and the five chlorine atoms are all held by ordinary covalencies. The polar formula (V) which was first suggested by Langmuir,[4] enables the octet rule to be maintained, but assumes that phosphorus is tetracovalent in the form of a positive $PCl_4{}^{\oplus}$ ion, and that the remaining chlorine is held by electrostatic attraction as in ammonium chloride. The last of these, (VI), represents three chlorine atoms held to phosphorus by ordinary covalencies and two labile chlorine atoms held by singlet linkages, and was first suggested by Prideaux in 1923, and later used by the Ingolds in 1926 for the purpose of explaining the behaviour of phosphorus pentachloride in aromatic substitutions.


$Cl:\underset{Cl\;Cl}{\overset{Cl\;Cl}{P}}$

(IV)

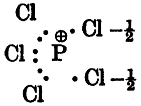

$\left[Cl:\underset{Cl}{\overset{Cl}{P}}:Cl\right]^{\oplus}\overset{\ominus}{Cl}$

(V)


$Cl:\underset{Cl}{\overset{Cl}{P}}\begin{matrix}\cdot\,Cl)^7\\ \cdot\,Cl)_7\end{matrix}$

(VI)

The objection to the formula (IV) is that it necessitates abandoning the octet rule which is supported by so much chemical and physical evidence. Furthermore, if the octet can be expanded to a group of ten electrons, the obvious question which arises is why the semipolar double bond in phosphorus oxychloride does not go over to an ordinary non-polar link by a similar process of expansion of the valency group to ten; particularly, since the positive charge on the phosphorus atom must exert a considerable attraction on the unshared electrons of the oxygen atom. The fact that this does not occur, indicates clearly that there is considerable resistance to an expansion of the octet of phosphorus. The electrovalent formula (V), although it enables the octet rule to be maintained, does not accord well with the properties of phosphorus pentachloride, which strongly suggest a covalent character. It is true that a small conductivity has been observed for a solution of phosphorus pentachloride in nitrobenzene, but transport measurements have shown that the phosphorus atom moves *towards the anode*, so that the ions are most probably formed by combination with the solvent. The formula (VI) suggested by Prideaux,[5] on the other hand, agrees very well with the properties of phosphorus pentachloride such as its ready thermal dissociation into the trichloride and chlorine, and its behaviour in aromatic substitution. It must be noted, however, that this formulation implies the presence of half negative charges on each of the labile chlorine atoms and an effective positive charge on the phosphorus atom which is acting as a donor; the singlet linkages are indeed really *semipolar single bonds.*



$$\begin{array}{l} \mathrm{Cl} \\ \;\;\cdot\!\cdot\,\overset{\oplus}{}\cdot\,\mathrm{Cl}-\tfrac{1}{2} \\ \mathrm{Cl}:\mathrm{P} \\ \;\;\cdot\!\cdot\quad\cdot\,\mathrm{Cl}-\tfrac{1}{2} \\ \mathrm{Cl} \end{array}$$

(VII)

These half charges do not, of course, imply the splitting of an electron—but are merely interpreted on a dynamical basis, on the lines of Højendahl,[6] as a statistical average obtained by integrating the field of the electron in the neighbourhood of a particular atom, over a time period which is large compared with the period of revolution of its orbit.

Strong evidence in support of the semipolar single-bond formula for both phosphorus pentachloride and antimony pentachloride has been provided by Sugden's [7] measurements of the parachor of these compounds. Now in making parachor calculations, the duplet or ordinary covalency is taken as zero, and in the non-polar double and triple bonds each electron in excess of this adds 11·6 units to the parachor. As Sugden points out, it is therefore highly probable that the singlet link, with one electron less than the duplet link, would cause a diminution of 11·6 units in parachor. The fact that the singlets in phosphorus pentachloride are essentially semipolar single bonds necessitates, however, a further diminution in parachor, which should be half that associated with a semipolar double bond. The latter is known to be − 1·6, and the parachor of a singlet semipolar linkage would therefore be expected to be

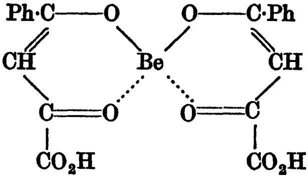
$$-\left(11{\cdot}6+\frac{1{\cdot}6}{2}\right)=-12{\cdot}4.$$

It will be seen that the parachors of phosphorus pentachloride and antimony pentachloride are in excellent agreement with the singlet formulæ :

Compound	[*P*] *observed*	[*P*] *calculated for 2 singlets*
Phosphorus pentachloride .	282·5	284·4
Antimony pentachloride .	311·8	312·7

The calculated values for the parachors of these substances on the supposition of the expansion of the octet to a valency shell of ten electrons are, of course, very much higher indeed (PCl_5, 316·9 ; $SbCl_5$, 345·2), and the parachor measurements therefore provide very strong evidence indeed of the singlet formulæ for these higher halides.

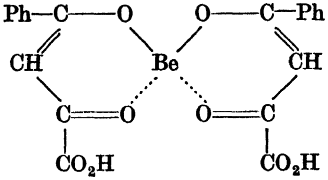
Sugden has also applied the theory of singlet linkages to the formation of chelated metallic derivatives of diketones and similar compounds in a very interesting way. The resolution of the beryllium compound of benzoylpyruvic acid by Mills and Gotts indicates that the four linkages to beryllium, including the two residual valencies, which are written with dotted lines in formula (VIII), must have a tetrahedral configuration.

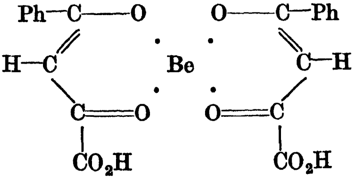


(VIII)

In Chapter IV, these two residual valencies were represented, following Sidgwick, as co-ordinate links in which the oxygen atoms acted as donors and the beryllium atom as acceptor. This involves an unusual distribution of polarities since oxygen becomes thereby positively charged, while the metal atom acquires negative polarity, and Sugden suggests an alternative formula which is obtained by splitting the duplet link between beryllium and oxygen in (VIII) to give a singlet to each oxygen as in (IX).

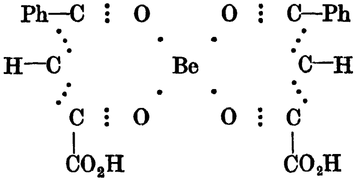
(VIII)





(IX)

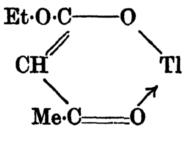
The small positive and negative charges on the oxygen atoms can then be smoothed out by rearranging the electrons in the rest of the ring as triplet electronic linkages, giving the symmetrical formula (X) in which every atom is neutral.

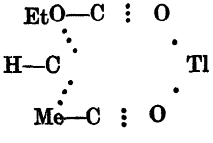


(X)

The parachors of several compounds of this type have been determined by Sugden,[8] and the case of ethyl thalloacetoacetate may be taken as typical. The observed parachor for this chelated compound is 332·2. The sum of the parachor equivalents for Sidgwick's co-ordinated formula (XI), excluding the thallium atom, is 293·6, whereas that for the singlet linkage formula (XII) is 272·0. This gives the atomic parachor of thallium as 38·6 if the co-ordinated formula is correct, and as 60·2 if ethyl thalloacetoacetate has the structure (XII).

(XI)





(XII)

An examination of the parachors of thallous ethoxide, thallous formate, and thallous acetate, in which the question of singlet linkages does not arise, however, gives an average value of about 65 for the atomic parachor for thallium, in accordance with the singlet formula (XII) for the acetoacetic ester derivative.

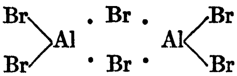
Further evidence in favour of the application of the theory of singlet linkages to chelated compounds appears to be furnished by the examination of the parachors of beryllium acetylacetonate, its propionyl homologue, and the basic propionate of beryllium. Sidgwick's duplet formulæ for these compounds leads in all three cases to negative values for the atomic parachor of beryllium, which cannot of course be accepted. The average value for the atomic parachor of beryllium calculated on the basis of the singlet formulæ is, however, 37·8, which lies between the values found for the atomic parachors of lithium and boron.

Compound	*Parachor* (observed)	*Be* (calculated on singlet formula)	*Be* (calculated on duplet formula)
Beryllium acetonylacetonate	470·4	44·4	— 2·0
Beryllium propionylacetonate	539·0	35·0	— 11·4
Beryllium propionate (basic)	985·4	34·0	— 12·4

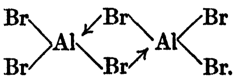
The cases of the acetylacetonate and the propionylacetonate of aluminium are similar, a negative value for the atomic parachor of aluminium being indicated by Sidgwick's duplet formulæ. The average value obtained on the basis of the singlet formulæ for these compounds and for aluminium bromide, is 38·6, which lies between the constants for sodium and silicon.

Compound	*Parachor* (observed)	*Al* (calculated on singlet formula)	*Al* (calculated on duplet formula)
Aluminium acetonylacetonate	680·5	41·5	— 28·1
Aluminium propionylacetonate . . .	788·0	32·0	— 37·6
Aluminium bromide * (Al_2Br_6)	457·6	42·2	21·6

* The atomic parachor for aluminium is calculated in the case of the bromide on the basis of the singlet formula

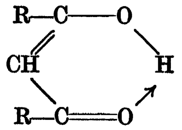


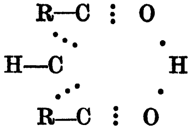
and the duplet structure



It has been suggested that β-diketones possess chelated cyclic structures involving co-ordinated hydrogen (XIII). Formulæ of this type are, of course, open to the objection already referred to (p. 30) that the K level cannot contain more than two electrons without the violation of the Pauli principle. This does not apply to the singlet formula (XIV), but actually the determination of

(XIII)



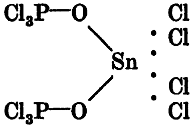


(XIV)

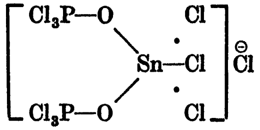
the parachor of typical members of the group indicates that these compounds have the ordinary open-chain structure $R{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}R$.

Compound	[*P*] observed	[*P*] calculated for open chain
Acetylacetone . . .	245·4	247·2
Propionylacetone . . .	279·7	286·2
Benzoylacetone . . .	382·4	381·1

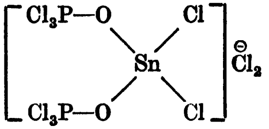
Sugden[9] has also applied the theory of singlet linkages to explain the formation of certain molecular compounds, amongst which may be mentioned the double compound of stannic chloride and phosphorus oxychloride $SnCl_4{\cdot}2POCl_3$. This is a well-defined crystalline substance melting at 54° and boiling at 118°, and possessing the properties of a typically covalent compound. The three possible electronic structures for the substance, assuming that it is impossible for the outer electron sheath of the tin atom to expand beyond the octet, are shown below with the predicted values for the parachors:



[P.] calc. 665·4
(XV)



[P.] calc. 688·6
(XVI)

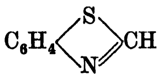


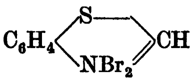
[P.] calc. 711·8
(XVII)

In the first of these, the four chlorine atoms in stannic chloride become linked by singlets, the lone pairs from the oxygen atoms of the phosphorus oxychlorides being thereby accommodated without expansion of the octet. In the other two formulæ (XVI and XVII) singlets are replaced by polar bonds, but an examination of the double compound by Garner and Sugden has shown that it is not only readily soluble in hydrocarbon solvents, but that the electrical conductivity of the fused compound is very low indeed (the specific conductivity is less than 8×10^{-5} mhos at 60°). These formulæ are therefore excluded, but the observed parachor for the compound, 689·7, is considerably higher than the value calculated for the presence of four singlet linkages as in formula (XV). This is explained by Sugden on the assumption that the *solid* substance has this formula, but that it undergoes appreciable dissociation into the original components on fusion, and this is supported by the fact that on distillation of the compound a certain amount of decomposition actually does take place; the first fractions containing an excess of the more volatile stannic chloride.

Singlet linkages have also been used by the author and his collaborators in explaining the formation of bromo-addition compounds of heterocyclic bases of the type of pyridine and benzthiazole.[10] Thus, benzthiazole itself (XVIII) gives rise to a well-defined dibromide (XIX), in which the labile bromine atoms are linked to the nuclear nitrogen atom.

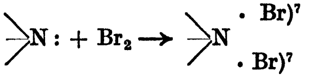
(XVIII)





(XIX)

Since the fifth valency of nitrogen in normal compounds is always an electrovalency, it follows that the labile bromine atoms in such compounds must be attached to the nitrogen atom by singlet linkages:



$$>N: + Br_2 \longrightarrow >N\begin{matrix} \cdot\, Br)^7 \\ \cdot\, Br)^7 \end{matrix}$$

This is in excellent agreement with the properties of the compounds such as their colour, thermal dissociation, and their tendency to pass into the hydrobromides of bromo-substituted bases; a reaction which is readily understood on the basis of a reversion to the more conventional ammonium structure.

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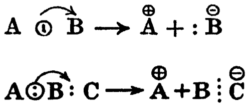
CHAPTER VIII

THE THEORY OF AROMATIC SUBSTITUTION

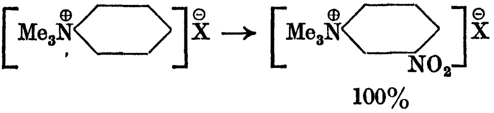
One of the most important applications of the Electronic Theory of recent years has been in connexion with the light which it has thrown on the classical problem of the effect of substituents on aromatic substitution. It is well known that the Alternation of Affinity Theory of Flürscheim and Vorländer's theory of polarised atoms, although they have frequently proved remarkably successful in interpreting the effect of substituents on aromatic substitution, often lead to inconsistencies. For instance, obvious difficulties are presented by the fact that, whatever may happen within the benzene ring itself which can be interpreted either on the lines of alternation of affinity or alternation of polarity of the atoms of the aromatic nucleus itself, there is frequently a definite absence of alternation in the side-chain attached to an aromatic nucleus. Before discussing the electronic interpretation of the phenomena of aromatic substitution it is, however, necessary to refer to the electronic interpretation of changes in the molecular structure of compounds.

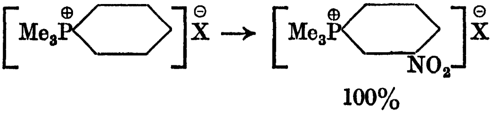
There are two chief ways in which a compound can undergo decomposition, namely, by ionisation and by a retrograde 1 : 2-addition, which correspond electronically with the appropriation of a duplet either by a single atomic nucleus, or two nuclei acting in conjunction :

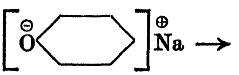


A predisposition to reactivity can be attributed to a force acting on a given duplet in such a way that it would move it in one of the directions indicated in the diagram above ; the electronic orbits being slightly displaced in these directions. Small shifts of such a type alter the screening action of the electron groups surrounded by adjacent atomic nuclei, giving rise to a reactivity which can be propagated from one atom to another along a chain. A frequent origin of disturbances of this type lies in the unequal covalent sharing of electrons by unlike atoms, with the result that a substituent in a hydrocarbon chain, for instance, creates forces which attract or repel neighbouring electrons from the α-carbon atom X —<— C or Y —>— C, as is indicated by the creation of small dipoles (see Chapter V).

Adopting the view that chemical reactivity is due to loosely held electrons, it is apparent from the speed of *ortho-para* substitutions as compared with the slowness of *meta* substitutions, that groups which direct *ortho-para* in aromatic substitution are associated with a *repulsion* of certain electrons of the benzene nucleus, while *meta*-directing substituents are associated with an *attraction* of electrons from the aromatic nucleus. This agrees with the known orienting effect of charged atoms whose action on the electrons is more or less independent of the theory of stable valency groups, and can be deduced directly from the sign of the charge, in that positive and negative poles* represent the most powerful known *meta* and *ortho-para* directing influences. Thus the positive poles in trimethylphenylammonium and trimethylphenylphosphonium ions cause 100 % *meta* nitration under the usual conditions, whilst the negative poles in phenoxides and thiophenoxides cause exclusive *o-p*-substitution in phenols and thiophenols in alkaline solution :







Exclusive *o-p*-substitution.

Now if we regard *ortho-para* substitution as being caused by the formation of residual affinities, consisting of loosely held electrons, at these positions, the electronic interpretation will be that, relative to hydrogen, an *o-p*-directing group X allows its electrons to come more under the influence of the positive atomic nucleus of the adjacent carbon atom of the benzene nucleus, with a corresponding loss of control of electrons which are held by this carbon atom in conjunction with the *ortho* carbon atom [1]:

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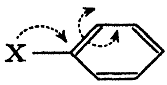
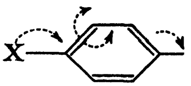
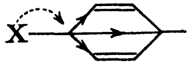
* The seat of a charge in a complex ion is termed a "pole."



Reactivity at the *para* position can be developed by mutually accommodating adjustments of electrons from the two double bonds of the Kekulé phase:

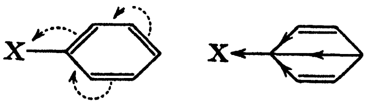


but as Ingold [2] pointed out some years ago, a more satisfactory interpretation appears to be furnished by the conception of direct *para*- affinity exchange by means of the Dewar phase of the benzene nucleus:



The Dewar phase is indeed a most satisfactory means for expressing the ease with which electrical disturbances reach the *para* position in view of the fact that orienting influences are known to suffer severe damping in passing through double linkages in side-chains attached to aromatic nuclei.

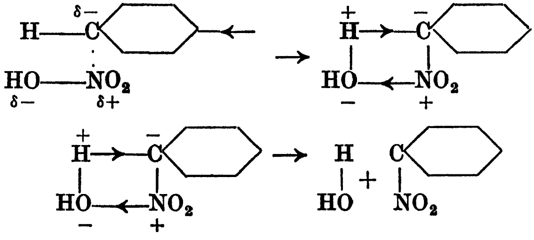
With regard to *meta* substitution, it must be again emphasised that whilst *ortho-para* substitutions are often almost instantaneous at ordinary temperatures, *meta* substitutions are notoriously slow, and probably the best conception is that *meta* substitution is a *residual effect* produced by the disappearance of free affinity from the *ortho* and *para* positions, which may arise from a reversal of the electronic processes suggested for *ortho-para* substitution:



m-Orientation.

This explains why it is that in the absence of other influences, a weak *o-p*-directing group outweighs a strongly *meta* directing group in competition, and why further substitution in a mononitrated naphthalene occurs in the unsubstituted aromatic ring.

If the theory of residual affinities due to loosely held electrons as the origin of *ortho-para* substitution is accepted it is clear that after the preliminary attachment of the reagent molecule has occurred, some much more powerful factor must operate which carries the process of nuclear substitution to completion by a comparatively direct route. This can be most readily illustrated by the case of nitration. Here it is evident that the *driving force* behind the process must be the tendency for hydrogen and hydroxide ions to unite to form undissociated water molecules, and the process of *para* substitution by the nitro group in a monosubstituted benzene can be visualised as follows.—First, the fractional charge which can be symbolised $\delta -$ at the *para* carbon atom, produced by the loosening of electrons at this point, attracts the fractional positive charge $\delta +$ of the nitrogen atom of the nitro group in the nitric acid molecule with the production of a state of affairs which can be represented as I → II. The tendency of hydrogen and hydroxyl to form undissociated water then operates and drives the process to completion (II → III), with the production of the *para* nitro derivative [3]:


(I) (II)

(II) (III)

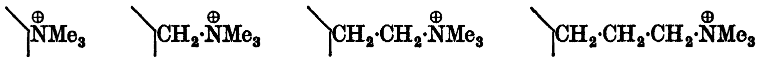
Other aromatic substitutions can be pictured in a similar manner, and it is possible that the reason why hypochlorous acid chlorinates more readily than it oxidises aromatic compounds is that the tendency to form undissociated water is greater than the tendency to form ionising hydrogen chloride.

This picture of aromatic substitution assumes the preliminary addition of an *incipiently* ionised molecule. The other alternative to this is to assume that a small part of the reagent is fully ionised and that the attack is made by the positive ion of the reagent molecule. As regards its face value, this appears to be quite a reasonable hypothesis since there are recorded cases of nuclear attack by positive ions such as the diazonium ion. As far as chlorination by hypochlorous acid is concerned, however, this problem has been definitely settled by Soper and Smith,[4] who have shown by dynamical methods that in the chlorination of phenol the reaction takes place between the phenoxide *ion* and the hypochlorous acid *molecule.*

With regard to the directive effect of different groups in aromatic substitution, the first effects which have to be considered are those of the seats of positive and negative electricity in organic ions, which are termed *positive* and *negative* poles respectively.

Positive Poles.—The directive effect of a positive pole directly attached to a benzene nucleus is as was first shown by Vorländer in 1919,[5] essentially *meta* directing. The best-known examples are probably the bromination of phenyltrimethylammonium bromide, the nitration of phenyltrimethylammonium nitrate,[6] of triphenylhydroxyphosphonium nitrate,[7] triphenylantimony dinitrate,[8] triphenylbismuth dinitrate,[9] and of diphenyllead nitrate. In all these cases, the directive effect of the positive pole is substantially the same, although the atomic weight and electrochemical character varies from nitrogen to lead.

The introduction of saturated carbon atoms such as those of CH_2 groups, between a positive pole and the benzene ring causes a damping out of the *meta* directive effect. Thus ionised benzylammonium salts are nitrated largely, but not completely, in the *meta* position,[10] while β-phenylethylammonium salts undergo *meta* nitration to a somewhat more limited extent and γ-phenylpropylammonium salts are nitrated in the *meta* position to a still lesser extent than the phenylethylammonium salts.[11] The experimental figures for *meta* nitration in a series of compounds of this type are as follows:



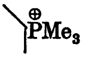
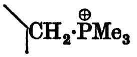
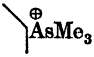
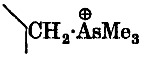
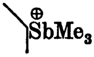
$\overset{\oplus}{N}Me_3$ 100%

$CH_2{\cdot}\overset{\oplus}{N}Me_3$ 88%

$CH_2{\cdot}CH_2{\cdot}\overset{\oplus}{N}Me_3$ 19%

$CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{\oplus}{N}Me_3$ 5%

The part of the electrostatic force which promotes *meta* nitration is that which reaches the aromatic ring through the enveloping screen of electrons, and consequently increasing the atomic number of the charged atom would be expected to diminish the *meta* directive force, since each successive sheath of electrons would be expected to weaken this effect. This is actually the case as is shown by a comparison of the nitration of phosphonium, arsonium, and stibonium salts; the figures for *meta* nitration in the case of these positive poles being as follows[12]:

 $\overset{\oplus}{P}Me_3$ 100%	 $CH_2{\cdot}\overset{\oplus}{P}Me_3$ 10%	*meta* nitration
 $\overset{\oplus}{As}Me_3$ 98%	 $CH_2{\cdot}\overset{\oplus}{As}Me_3$ 3·4%	,, ,,
 $\overset{\oplus}{Sb}Me_3$ 86%		,, ,,

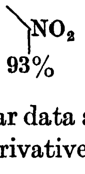
From these figures it is seen that the attraction of the aromatic electrons by the positive pole is decreased with relay through intervening saturated carbon atoms, and furthermore that the portion of the positive electrical field which reaches through the surface of the charged atom and is available for the creation of orienting effects is smaller the larger the size of the positively charged atom. In other words, the octets of the carbon atoms which separate the positive pole from the benzene ring, and the outer sheaths of electrons of the larger charged atoms form two different types of electron screen through which the positive field may become damped in its passage to the aromatic nucleus.

A further illustration of this is furnished by the recent direct comparison of the nitration of phenyl and benzyl sulphonium and selenonium salts, for which the percentages of *meta*-substitution are as follows[13]:

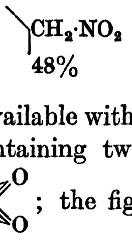
$Ph{\cdot}\overset{\oplus}{S}Me_2$	$Ph{\cdot}CH_2{\cdot}\overset{\oplus}{S}Me_2$
100%	52%
$Ph{\cdot}\overset{\oplus}{Se}Me_2$	$Ph{\cdot}CH_2{\cdot}\overset{\oplus}{Se}Me_2$
100%	16%

Negative Poles.—The effect of a negative pole is essentially *ortho-para* directing, and has long been illustrated by the rapid and exclusive *ortho-para* substitution of phenols and thiophenols in alkaline solution. There do not appear to be any simple examples of the probable decrease in *o-p-* directive effect produced by increasing the distance between the negative pole and the benzene nucleus by intervening carbon atoms, although attention may be drawn to the fact that benzyl mercaptan has never been observed to couple with diazo salts, nor has it been observed to undergo *o-p*-substitution in alkaline solution.

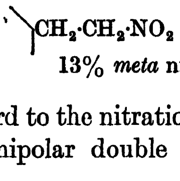
Semipolar Linkages.—Considerable interest attaches itself to the effect of semipolar linkages, which behave very much in the manner which would be expected of an ionic charge of a free pole corresponding with the end of the dipole nearer the nucleus, but somewhat weakened by the partly compensating opposite effect of the more distant pole of opposite sign. That is to say, that the nitro group, for instance, has the effect of a positive pole attached to the benzene ring somewhat inhibited by the negative charge on the oxygen atom of the semipolar double bond. Thus nitrobenzene undergoes *meta* substitution to the extent of 93%, and the effect of inserting saturated carbon atoms in the form of CH_2 groups between the nitro group and the benzene nucleus is as might be anticipated, to further diminish the effect of the positive charge on the nitrogen atom; the figures for *meta* nitration in phenylnitromethane and *β*-phenylnitroethane being as follows [4]:



93%

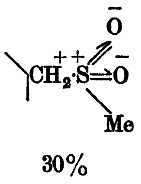


48%

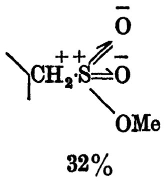


13% *meta* nitration.

Similar data are available with regard to the nitration of sulphonic acid derivatives containing two semipolar double bonds in the sulphone group $-\mathrm{S}\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow \mathrm{O}}$; the figures for the proportion of *meta*-nitration in the cases of the sulphone and sulphonic esters being as follows:

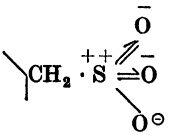


30%



32%

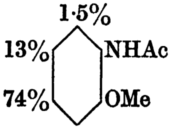
In both these cases, the partial compensation of the *meta* orienting effect of the charged sulphur atom arises from only two negatively charged oxygen atoms, but in the sulphonic acid, ionisation introduces a third negatively charged oxygen atom equivalent in all respects to the other two

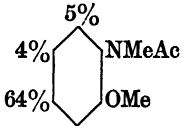


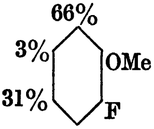
with the result that there is a drop to 14% in the proportion of the *meta* compound formed on nitration of this acid.

Neutral Systems.—In discussing neutral systems, the basic principle is that *it is possible to carry over to all substituents the conclusions which have been deduced for poles and polar linkings*; that is to say, that the repulsion of aromatic electrons leads to *o-p-* substitution, and the attraction of electrons to *meta* orientation.

With regard therefore to the directive effect of groups which do not contain poles, it is obvious that their orienting effects will naturally be dominated by their constitution, and it is well known that groups which are attached to a benzene nucleus by means of atoms which possess lone pairs of electrons lead to *o-p-* substitution. With neutral nitrogen, oxygen, and fluorine atoms, which belong to this class and which contain the same number of electrons when they are in the combined state, it has been shown by the nitration of the following compounds [15]:







in which the relative attack at the different positions in the aromatic nucleus is indicated, that *o-p-* directive power runs parallel with the degree of activity of the unshared electrons. That is to say that, the *o-p-* directive power decreases with increasing atomic number, which means increasing strength of nuclear charge; nitrogen having greater *o-p-* orienting power than oxygen, which in turn has greater orienting power than fluorine. This sequence N > O > F, it may be noted, is the reverse from that which would have been predicted from the theory of alternate polarities, which would presumably require the most electronegative element to create the strongest *o-p-* nuclear negative polarity: F > O > N.

For neutral elements of the same periodic group, the electron affinity should diminish with increasing size just as with positively charged elements, and this is borne out by the proportion of *meta* nitration occurring in benzyl halides[16] :

$\diagdown CH_2 \rightarrow F$	$\diagdown CH_2 \rightarrow Cl$	$\diagdown CH_2 \rightarrow Br$
17·5%	15·5%	6·9%

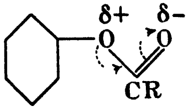
It has been shown that replacement of hydrogen by methyl causes a recession of electrons from the substituent, which is the reverse of the comparatively powerful effect of the opposite kind produced by the substitution of chlorine for hydrogen (p. 52); the signs of the molecular moments of toluene and chlorobenzene being:

$$(-)\ \mathrm{Ph} \longleftarrow \mathrm{Me}\ (+) \qquad (+)\ \mathrm{Ph} \longrightarrow \mathrm{Cl}\ (-)$$

The effect of *alkyl groups* is therefore to promote, though not very powerfully, *o-p-* substitution, and similar substitution has also been observed to occur when hydrogen is replaced by a tetracovalent silicon atom. There is therefore good reason to suppose that these atoms allow their shared electrons to be controlled by the nucleus of the attached carbon atom to a greater extent than a hydrogen atom would permit in similar circumstances, and this effect of increasing the *o-p-* directive effect, or of decreasing the *meta* directive effect, by replacing hydrogen by alkyl groups is well illustrated by the nitration of the benzoic esters, which yield the following proportions of *meta* nitro derivatives[17] :

$Ph{\cdot}CO_2H$	$Ph{\cdot}CO_2Me$	$Ph{\cdot}CO_2{\cdot}CH_2Me$	
80·2%	73·2%	68·4%	meta nitro derivatives.

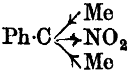
As is fairly well known, *acyl groups* have the opposite sort of effect; that is to say, they cause an enhancement in *meta* orienting power and a decrease in *o-p-* substitution. It is possible to explain this on the basis of a partial appropriation of electrons by the carbonyl oxygen atom, which confers partial dipolar character on the phenyl esters, which, although it may not be strong enough to bring about *meta* substitution, tends to oppose the *o-p-* orienting movement of the lone electrons:



The attachment of halogen atoms to the carbon atom next to the aromatic nucleus produces, on account of the high electron affinity of halogen atoms and the stability of their ions, a tendency towards *meta* substitution, as is shown by the nitration of benzyl chloride, benzal chloride, and benzotrichloride:

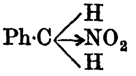
$Ph{\cdot}CH_2Cl$	$Ph{\cdot}CHCl_2$	$Ph{\cdot}CCl_3$
15·5%	35%	64% *m*-nitration.

The effect is indeed the reverse of that of alkyl groups, which is strikingly illustrated by the introduction of methyl and bromine in place of hydrogen atoms of the somewhat strongly *meta* directing nitromethane group—$CH_2{\cdot}NO_2$:



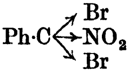
$$\mathrm{Ph{\cdot}C}\begin{matrix}\swarrow \mathrm{Me}\\ \rightarrow \mathrm{NO_2}\\ \nwarrow \mathrm{Me}\end{matrix}$$

(*meta*, 29%)



$$\mathrm{Ph{\cdot}C}\begin{matrix}/ \mathrm{H}\\ \rightarrow \mathrm{NO_2}\\ \backslash \mathrm{H}\end{matrix}$$

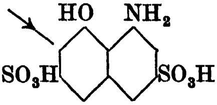
(*meta*, 50%)



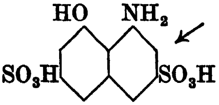
$$\mathrm{Ph{\cdot}C}\begin{matrix}\nearrow \mathrm{Br}\\ \rightarrow \mathrm{NO_2}\\ \searrow \mathrm{Br}\end{matrix}$$

(*meta*, 84%)

A point which must not be lost sight of in considering the orienting power of groups is the tendency to *ion formation.* As has been pointed out by Ingold, apparent exceptions to the N > O > F rule are traceable either to *ionisation* of a phenolic hydroxyl group or to *salt-formation* by a basic grouping; thus phenols tend to substitute through their anions, and aniline derivatives through their neutral forms, even when very little of these reactive forms are present. For instance, H acid is known to couple at the point shown in alkaline solution:



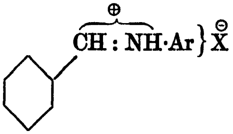
but at the point:



in feebly acid media. The complete theoretical sequence of *o-p*-directive power for neutral and charged oxygen and nitrogen is:

$$\overset{\ominus}{O} > NR_2 > OR > \overset{\oplus}{N}R_3.$$

When a ψ-basic system is present as in the Schiff's bases derived from benzaldehyde, salt formation should produce marked *meta* orientation owing to the ready transference of the cationic charge to the atom adjacent to the ring. It has been shown by Baker and Ingold [18] that Schiff's bases are present in sulphuric acid as salts of the type:



which undergo almost exclusive nitration in the *meta* position.

Particular interest attaches itself to the directive effect of triple linkings. In contrast to the exclusive *o-p-* nitration of cinnamic acid, it has been found that phenylpropiolic acid, $Ph{\cdot}C{\equiv}C{\cdot}CO_2H$ yields 8% of the *meta* nitro derivative on nitration at − 30°. In explaining this, Baker, Cooper, and Ingold [19] have made the assumption which it is not yet possible to *explain*, that when six valency electrons are mutually shared by two atomic nuclei, the system tends to appropriate additional electrons in order to form a stable association of eight, or, if possible, ten electrons. The appropriation, it is assumed, may be complete or incomplete, and may affect two or four shared or unshared electrons, but in most cases it is incomplete. This conception was foreshadowed by Langmuir [20] in 1919 in his model of the nitrogen molecule, which corresponds to the special case of the complete appropriation of four unshared electrons.

Now the appropriation of unshared electrons belonging to either or to both combined atoms will be accompanied by a loss of basic character, and the appropriation of shared electrons results in a tendency towards ionisation and tautomerism. Owing to the lability of the unshared electrons of the tervalent nitrogen atom, the effect reaches a maximum when these can be absorbed, and nitrogen therefore with its electronic group of ten, and nitriles with their electronic group of eight are non-basic, although according to ordinary electronic formulation they contain the unshared electrons of a reactive tertiary amine:

$$:\overset{\curvearrowright}{N}:::\overset{\curvearrowleft}{N}: \qquad R{-}C:::\overset{\curvearrowleft}{N}:$$

When the electrons which are required to form the stable group of eight or ten electrons are shared with hydrogen, the inherent tendency of the latter to pass into the cationic state co-operates in favour with ionisation, and we therefore find that in hydrocyanic acid and the alkylacetylenes one hydrogen atom is replaceable by metals.

$$\mathrm{H:\overset{\curvearrowright}{C}:::\overset{\curvearrowleft}{N}:}\qquad\qquad \mathrm{R{-}C:::\overset{\curvearrowleft}{C}{-}H}$$

When the shared electrons bind together atoms other than hydrogen, different results are observed. For instance, diazonium salts decompose much more readily than quaternary ammonium salts because the quaternary group in diazonium salts has an enhanced power of withdrawing electrons from the neighbouring hydrocarbon radical:

$$\left[\mathrm{R{-}\overset{\curvearrowright}{\overset{\oplus}{N}}{\equiv}\overset{\curvearrowleft}{N}:}\right]\overset{\ominus}{\mathrm{X}} \rightarrow \overset{\oplus}{\mathrm{R}} + \mathrm{N_2} + \overset{\ominus}{\mathrm{X}} \rightarrow \mathrm{RX} + \mathrm{N_2}$$

$$\left[\mathrm{R{-}\overset{\oplus}{N}Alk_3}\right]\overset{\ominus}{\mathrm{X}} \rightarrow \overset{\oplus}{\mathrm{R}} + \mathrm{NAlk_3} + \overset{\ominus}{\mathrm{X}} \rightarrow \mathrm{RX} + \mathrm{NAlk_3}$$

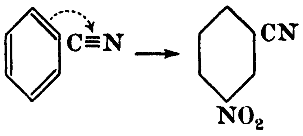
A similar explanation can be applied to the ready decomposition of acetylenic acids into carbon dioxide and acetylenes on heating:

$$\mathrm{RC\overset{\curvearrowleft}{\equiv C}{-}CO\overset{\curvearrowleft}{-O}{-}H} \rightarrow \mathrm{RC{\equiv}CH} + \mathrm{CO_2}$$

which is analogous to the thermal instability of the β-ketonic acids:

$$\mathrm{\overset{\curvearrowleft}{O{=}}CR\overset{\curvearrowleft}{-CH_2}{-}CO\overset{\curvearrowleft}{-O}{-}H} \rightarrow \mathrm{O:CR{\cdot}Me} + \mathrm{CO_2}$$

The high acidity of acetylenic acids in contrast to the corresponding saturated or olefinic acids is also to be explained on similar lines. In phenylpropiolic acid, for instance, part of the electron affinity of the triple bond is occupied in assisting the ionisation of the carboxyl group, and the rest of it exerts an attraction on the aromatic electrons, which leads to *meta* substitution. The strong *meta* directive power of the cyano group is also partly attributable to the same cause:



Mechanism of Transmission of Orienting Effects.—With regard to the problem of the mechanism of transmission of orienting effects in the aromatic nucleus it is first necessary to define the types of electrical displacement which are possible in connexion with the phenomena. As has already been pointed out, a substituent in a hydrocarbon chain, due to unequal covalent sharing of electrons by unlike atoms, must create forces which attract neighbouring electrons towards the depleted α-carbon atom $\mathrm{X{-}\!\leftarrow\!{-}C{-}\!\leftarrow\!{-}C{-}\!\leftarrow\!{-}C}$, or repel them from the surfeited carbon atom, $\mathrm{Y{-}\!\rightarrow\!{-}C{-}\!\rightarrow\!{-}C{-}\!\rightarrow\!{-}C}$. This effect will be relayed with diminishing intensity along the chain by induction, and has been therefore described by Ingold[21] and his collaborators as the "*inductive*" effect (*I*). It is essentially a distortion of the electronic system, and a condition of strain which is a permanent condition of the molecule, capable of giving rise to an electrical moment which can be measured in the usual way.

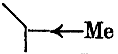
As soon as a chemical bond is identified with an electron duplet, it becomes clear that the double bonded displacements which for many years have been studied under the name of "tautomerism," $\mathrm{X{-}Y{=}Z \rightarrow X{=}Y{-}Z}$, are to be interpreted as electron duplet displacements, involving a redistribution of electrical charges:

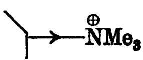
$$\mathrm{X{-}\overset{\curvearrowleft}{Y}{=}Z \longrightarrow X{=}Y{-}Z}$$

This type of displacement, in which *electrons whilst remaining in one octet enter or leave another*, is regarded mainly as an isomeric change, rather than a permanent condition of the molecule, and has been termed the "*tautomeric*" effect (*T*), and incipient changes which if completed would be of this type are included in the classification and are represented by a dotted arrow $\curvearrowright$.

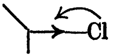
In addition to this, a substituent which is able to influence electron distribution by a mechanism involving relay through bonds of the types we have indicated, can also give rise to an electrical field which is also capable of acting on the molecule *directly through space*, and this has been named the "*direct*" effect of the substituent (*D*).

Toluene and the phenylammonium ion represent examples of the inductive effect acting in different directions, which can be symbolised thus:


(+ *I*)

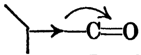

(− *I*)

Chlorobenzene, for instance, where there is a simultaneous attraction towards the halogen nucleus of *all* its electrons, shared and unshared, in addition to the normal sharing process between the lone halogen electrons and the attached carbon atom, represents a case in which both inductive and tautomeric effects of different sign occur:



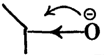
$(-I + T)$

The carbonyl group represents a case in which there will be a shifting of electrons towards the more electronegative element with the result that both inductive and tautomeric effects collaborate:



$(-I - T)$

In a similar way, the phenoxide ion represents a case in which both the inductive and tautomeric effects collaborate, but in the direction opposite to that in the carboxyl group:



$(+I + T)$

With regard to the transmission of the inductive effect in the aromatic nucleus, comparative measurements of the velocities of nitration of benzene and toluene indicate that the latter (type, $+I$) nitrates about fourteen times as quickly as the former.[22] From the proportions of the isomerides isolated, it follows that the reactivity of each *ortho* and *para* carbon atom in toluene is increased about 30 times owing to the presence of the nuclear methyl substituent, while the reactivity of each *meta* carbon atom is approximately doubled. It follows therefore that the methyl substituent in toluene primarily activates the *o*-*p*- positions, but that a small activation effect of a second order of magnitude also reaches the *meta* positions. The effect on the *meta* positions therefore reaches these carbon atoms by a less direct route. Correspondingly, it has been shown by velocity relations for the nitration of phenylammonium ions (type, $-I$) that the *o*-*p*- positions are strongly deactivated, while the *meta* positions are also deactivated, but to a lesser extent. This explains why the presence of a methyl·substituent in naphthalene promotes further substitution in the substituted nucleus, while a nitro or carboxyl group (type, $-I$) causes substitution in the adjacent ring.

Regarding the transmission of the tautomeric effect, an analysis of the type $(-I + T)$ requires an examination of the magnitude of the two effects, and a series corresponding to diminishing $+T$ and increasing $-I$ can be constructed and conveniently represented by Ingold's diagram [23]:

——diminishing $+ T$——>

(x) (y)

(*op*-orientation) } OAlkyl I Br Cl F $\overset{+}{\mathrm{I}}$Aryl { (*m*-orientation)

(nuclear activation) (x) (y) (nuclear deactivation)

——increasing $- I$——>

From the left to the point y beyond fluorine, the groups are *op*-orienting, but an examination of the relative velocities of nitration shows that the change over from nuclear activation to deactivation occurs at an earlier point x, between iodine and bromine. This indicates clearly that the tautomeric effect, unlike the inductive effect, is *not* relayed to the *meta* position. This leads to an important conclusion with regard to the conditions of excitation of the tautomeric effect, which does not arise in the case of the inductive effect, which is a permanent condition of the molecule which is measurable as the molecular electric moment, and in which the primary *op*- charges should be relayed to the *m*-carbon atom. If the effective *o*-*p*- charges produced by the tautomeric effect were really present, they could scarcely avoid a similar relay to the *meta* positions as in the case of inductive effect, and it must therefore be supposed that they are neutralised by the reagent as soon as they are produced. In other words, tautomeric displacements are excited by electron-seeking reagents, and therefore become of importance only at those moments when the reagent molecule is already committed to *ortho*- or *para*-substitution.

The direct effect only manifests itself in those cases where a decision is required between alternative substitutions which are nearly equally favoured by inductive and tautomeric effects. The fundamental conception is, of course, that the permanent electrochemical character of a substituent produces not only an inductive effect (I) relayed from bond to bond, but also has an action direct through space (*D*). The origin of the effect is therefore the same as that of the inductive effect, which it will follow in sign and magnitude in its variation from group to group, but once originated, however, its distribution will depend on distance and will therefore not be in the order of *op*- > *m*, but in the order *o* > *m* > *p*.

An illustration of the direct effect is provided by the nitration of the phenyl and benzyl halides in which the direct effect of the halogens should be a deactivating influence in the order:

$$F > Cl > Br > I$$

and the table, given hereunder, gives the values of the *para*- ½ *ortho*-ratio which shows the strong depression of *ortho*-reactivity due to the direct effect (— *D*) in fluorobenzene, and the smaller but lesser depressions shown by its analogues of higher molecular weight.

Halogen	F	Cl	Br	I
Ph·X . . .	13·76	4·64	3·30	2·85
Ph·CH_2·X . .	3·89	3·28	—	—

It may be noted that for the two benzyl compounds, the ratios are smaller than for their analogues in the phenyl series, but this is understandable since not only should the direct effect over the aromatic nucleus be smaller as a whole in the benzyl series, but also the ratio of the distances of the *o*- and *p*- positions from the halogen should be nearer unity. The interesting feature is that all these differences are in the direction opposite to those which might be predicted from the effect of steric hindrance.

With regard to the efficiency of attack of the aromatic nucleus by different reagent molecules there are, as has already been indicated in the picture for the mechanism of nitration (p. 78), two factors which have to be taken into account. Namely, the polarisation or capacity for polarisation of the attacking molecule, and secondly, the proton-affinity of the anionic portion which is ultimately eliminated in conjunction with the hydrogen of the aromatic nucleus. In the case mentioned, once molecular addition to negative carbon has taken place, it is the tendency of hydrion and hydroxide ion to form undissociated water which drives the process to completion.

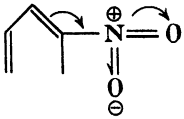
The operation of the first factor is most readily illustrated, however, by reference to halogenation.[24] Considerations of polarisation require that the activity of a chlorinating agent of the type X·Cl shall increase with the electron affinity of X, and similarly for bromination and iodination. This agrees with the fact that bromine monochloride although it is a powerful brominating agent does not chlorinate, and that iodine monochloride is a strong iodinating agent. The efficiency of halogenating agents is in the anticipated electron-affinity sequence: Cl > Br > I > OH, since chlorine is a more powerful chlorinating agent than hypochlorous acid, and bromine monochloride is a more powerful brominating agent than bromine, which in turn is more powerful than hypobromous acid.

On the other hand, it must be noted that hypoiodous acid is a more powerful iodinating agent than iodine, and this probably means that the second factor cannot be neglected. Iodine and hydroxyl are neighbouring members in the electron affinity sequence given above, and it is quite probable that the difference between the tendency for hydrion to combine with hydroxide ion to form feebly dissociating water and the slight tendency to the formation of readily ionising hydrogen iodide from its ions, outweighs the difference between the electron affinities of iodine and hydroxyl. As has already been pointed out (p. 78), it is highly probable that the reason why hypohalous acids halogenate more easily than they oxidise aromatic compounds is that the tendency to form undissociated water from hydrion and hydroxide ion is greater than the tendency to form ionising hydrogen halides.

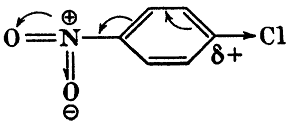
All this represents, of course, only one side of the picture of aromatic substitution, and mention must be made of the other side in which the atom to be replaced is not hydrogen, but an atom or group such as chlorine, which is most *stable as its negative ion*; the attacking reagent being of a positive-centre-seeking or basic type, such as NHRR′, $\bar{\text{O}}\text{R}$, $\bar{\text{S}}\text{R}$, etc. In this type of substitution, the orientation laws will have to be reserved as follows: The + *I and* + *D effects will be deactivating*, and the − *I and* − *D activating*. Their distribution over the ring will be: for ± I, *op* > *m*, and for ± D, *o* > *m* > *p*. The effect + *T*, which creates negative centres for reagents requiring them, therefore will not operate in this type, but another tautomeric effect, − *T*, which can create positive aromatic centres, will now come into play. This will arise at the demand of the reagent and will only act on the *op*- positions. The theoretical classification of groups on the basis of these principles for this type of aromatic substitution has been given by Ingold as follows:

Type	*Symbol*	*Examples*	*Effect*
1.	$+I$	$\overset{\ominus}{O}$, Me	*op*-deactivation, weaker *m*-deactivation.
2.	$-I$	$\overset{\oplus}{N}Me_3$, F	*op*-activation, weaker *m*-activation.
3.	$-I-T$	$\overset{+\ -}{NO_2}$, COR, NO, CN (also probably I, Br, Cl, SO_2R)	strong *op*-activation, much weaker *m*-activation.
4.	$+I-T$	CH : CRR′	*op*-activation indeterminate, weak *m*-activation.

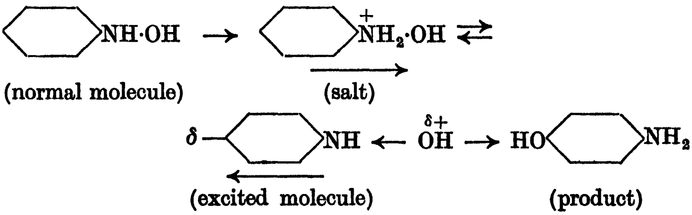
These types, although they have not been sufficiently studied for detailed consideration, are well illustrated by the nitro group. This should be a particularly powerful accelerator ($-I$, $-D$, and $-T$ effects), and should orient substitutions of the type discussed in *op*- positions:



The action of alkalis on the *op*- halogenated-nitrobenzenes which lead to ejection of halogen ion furnish familiar instances of this effect; the halogen being assumed to assist in the capture of the attacking negative ion by influence of its own attraction for the electrons of the carbon atom to which it is linked:



With regard to the fascinating cases of indirect substitution by migration, it may be noted that the conclusion that activating tautomeric displacements reach the *ortho-para* positions only, and that *meta* orientation always involves nuclear de-activation, explains why internal migrations from a side-chain to the nucleus invariably occur at the *ortho-* and *para*-positions. Internal migrations can occur only by a tautomeric electron-displacement which loosens a portion of the side-chain as a potential positive ion and simultaneously creates a negative *ortho*- or *para*-centre strong enough to attract and acquire it. Any reagent used to bring about such transformations can have only an *indirect* action in the process, depending presumably on the recoil of aromatic electrons suddenly released from forces which attract them to the substituent under the conditions of the reaction. This explains the reason why substituents which exhibit this phenomenon of indirect substitution by migration are invariably of a weakly *basic* character (for example, ·NHOH, NHAr, etc.), and why the catalysts are always acids. The process is best illustrated by Ingold's [25] picture for the transformation of phenylhydroxylamine into *p*-aminophenol. A hydrogen ion is first attracted to the basic nitrogen atom of phenylhydroxylamine, giving rise to loose ammonium salt formation with the production of a positive charge at this point which strongly attracts aromatic electrons. Next this added proton is removed by a hydroxylion when the released aromatic electrons spring back, creating simultaneously, negative *op*- charges by tautomeric displacements in the ring, and an electron-depleted hydroxyl group by mutually accommodating displacements in the side-chain. Thirdly, the positive hydroxyl group is drawn away by the electrical field present at one or more of the negative aromatic centres, and lastly the quinonoid aminophenols produced in this way, revert to their benzenoid forms by prototropic change. Shorn of most of its details, the process can be represented diagrammatically as follows :



A word of caution is necessary at this stage in that considerations of this type do not of course apply to *apparent* migrations, which are actually extra-molecular substitutions by a reagent formed by a previous decomposition such as the Chattaway-Orton rearrangements of *N*-chloroanilides into chloro-substituted anilides, in which the actual substituting agent is chlorine produced by decomposition of the *N*-chloro derivatives.

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CHAPTER IX

SIDE-CHAIN REACTIVITY

Some ten years ago, it was shown by Olivier [1] that a close "correspondence" exists between the factors which control nuclear reactivity in benzene derivatives and those which govern certain side-chain reactions in toluene derivatives. The simplest view which might be taken with regard to these side-chain reactions might be expressed by saying that a nuclear substituent which increases the nuclear reactivity in a given position, should also facilitate a reaction in a side-chain attached to that position, if the reaction depends, as regards speed, on the separation of a negative ion or the addition of a positive one. Conversely, that such a substituent should *inhibit* side-chain reactivity if the reaction involved depends on the addition of a negative ion or the separation of a positive one. A nuclear substituent which depresses nuclear reactivity by withdrawing electrons would be expected to act in the opposite way. This is not strictly accurate, but this view nevertheless provides the starting point for the consideration of the principles underlying aromatic side-chain reactivity from the standpoint of the electronic theory of chemistry.

Olivier's principle of correspondence is based mainly on an examination of the rates of hydrolysis of substituted benzyl chlorides in aqueous alcohol, and may be illustrated by the following coefficients, referred to benzyl chloride as unity:

HYDROLYSIS OF BENZYL CHLORIDES

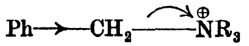
Substituent	*Velocity*
p- CH_3	10·6
o- CH_3	4·84
m- CH_3	1·39
p- Cl	0·62
o- Cl	0·355
m- Cl	0·237
p- Br	0·50

Substituent	*Velocity*
o- Br	0·286
m- Br	0·215
p- I	0·477
o- I	0·287
m- I	0·201
m- CO_2H	0·245
p- CO_2H	0·165
m- NO_2	0·090
o- NO_2	0·084
p- NO_2	0·074

It will be seen that the velocities of hydrolysis of the three isomers are in the order $o, p > m$, or $m > o, p$, according as to whether the substituent belongs to the *op*- or to the *m*- directing series. Furthermore, it will be observed that the facilitating or inhibiting action of the substituents exhibits a close parallelism with their influence on reactivity in ordinary aromatic substitution. Similar relationships have also been observed in other side-chain transformations such as in the condensation of benzyl chlorides with benzene in the presence of aluminium chloride, and in the hydrolysis of substituted benzoic esters.

These relations become, however, to a large extent inverted in another group of side-chain reactions. Thus Lapworth and Shoesmith[2] have observed that the two groups of nuclear substituents for which the ease of hydrolysis of isomeric benzyl halides are respectively in the order $o, p > m$ and $m > o, p$, become interchanged when the reaction studied is the reduction of benzyl bromides by hydriodic acid. Other examples of this phenomenon are also available which need not be discussed here, and it is therefore evident that there are two groups of side-chain reactions which are in some fundamental respect, the inverse of each other and this is the basis of Ingold's[3] classification of such reactions.

The fundamental classification is into two types, in the first of which, termed type A, an *influx* of electrons from the nucleus to the side-chain facilitates the change, and in the second of which, termed type B, a *recession* of electrons from the side-chain to the nucleus assists the change. Type A can be further subdivided into two sections, according as to whether the influx of electrons which assists these reactions are required to liberate a portion of the side-chain which carries all its electrons with it (type A_1), or to attract towards the side-chain an electron-seeking reagent (type A_2). The thermal fission of benzylammonium hydroxides which can be symbolised:



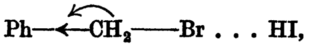
$$\mathrm{Ph}{-\!\!\succ\!\!-}\mathrm{CH_2}\text{———}\overset{\oplus}{\mathrm{N}}\mathrm{R_3}$$

and the hydrolysis of benzyl chloride, $\mathrm{Ph}{-\!\!\succ\!\!-}\mathrm{CH_2}\text{—}\mathrm{Cl}$ form illustrations of the first type (A_1), while the side-chain bromination of toluene

$$\mathrm{Ph}{-\!\!\succ\!\!-}\mathrm{CH_3}\ldots\overset{\delta+}{\mathrm{Br}}\cdot\overset{\delta-}{\mathrm{Br}}$$

furnishes an example of the second type (A_2), molecular bromine being an electron-seeking reagent.

A similar subdivision is also made with regard to the recession of electrons facilitating reactions of the type B, according as to whether this recession may assist either the partial or complete liberation of a group which abandons a previously shared electron pair (type B_1) or the electrostriction of a basic (positive-centre-seeking) reagent (type B_2). The reduction of benzyl bromide by hydriodic acid furnishes an example of the type B_1 and can be symbolised:



$$\mathrm{Ph}{-\!\!\prec\!\!-}\mathrm{CH_2}\text{——}\mathrm{Br}\ldots\mathrm{HI},$$

whilst the alkaline alcoholysis of benzyl chloride provides an example of the type B_2:

$$\mathrm{Ph}{-\!\!\prec\!\!-}\mathrm{CH_2{\cdot}Cl}\ldots\overset{\ominus}{\mathrm{O}}\mathrm{Et}.$$

As soon as a transformation has been classified as belonging to the type A, it becomes possible to apply the ordinary theory of aromatic substitution discussed in the previous chapter to the case, after making due allowance for the fact that the effects of nuclear substituents have to traverse not only the nucleus, but also part of the side-chain to reach the region of the reaction. Nuclear substituents have been classified into four groups in relation to ordinary benzene substitutions, *viz.* $+I$, $-I$, $-I+T$, and $+I+T$, and we may now consider what modifications of this are necessary in applying these principles to side-chain reactions of the A class. There are two modifications which have to be observed, namely, that owing to the small displaceability of the electrons in a single linking, selectively heavy damping will accompany the transmission of the tautomeric effect through side-chain single linkings to the point of the reaction, and secondly, the tautomeric effects should with additional damping in the nucleus, affect reactivity in *meta* side-chains.

With regard to the first of these, attention may be directed to the third group of substituents, symbolised $- I + T$, in which the inductive and tautomeric effects work in opposite directions. The inductive effect results in a deactivation whose extent will depend on the electron-affinity of the groups, whereas the tautomeric effect leads to activation depending on the tendency of the electrons to become shared. Now all the halogens possess considerable electron affinity in the neutral state, but iodine differs from the others in possessing considerable basic properties, as is shown by the formation of well-defined iodonium ions. It has been shown by Ingold and Shaw [4] that in nuclear substitution the tautomeric effect predominates in this halogen, whilst for the other halogens, the inductive effect is of primary importance. In Type A side-chain reactions, however, the tautomeric effect of iodine, due presumably to selective damping, no longer outweighs the inductive effect, with the result that iodine ranges itself along with the other halogens as a deactivating substituent, and furnishes a violation of Olivier's correlation principle.

The theoretical inferences underlying the fact that the effect of tautomeric polar influences on the reactivity of a *m*- side-chain should be definitely perceptible have been dealt with by Ingold and Patel [5] in connexion with their experiments on the aryl methyl bromides on the following lines :—In nuclear substitution, in which the reagent normally has the choice of exciting and thereafter utilising the tautomeric effects in those positions (*ortho*- and *para*-) in which they are primarily, and most easily stimulated, the orientation process is largely self-definitive—that is to say, the reagent becomes more and more irrevocably committed to *o*- or *p*-attack during its approach, from the moment it commenced to exert electrical action on the aromatic molecule until union is definitely accomplished. The result being that the $+ T$ effect, unlike the $+ I$ effect which is a permanent condition of the molecule, never leads to appreciable *meta*- substitution. A reagent which attacks a *m*- side-chain, on the other hand, has no alternative method of utilising an existing mechanism for tautomeric electron displacement within the nucleus than that of allowing the final stages of transmission of the effect of such displacements to proceed to the point of the reaction by ordinary induction. A substituent should thus, by its tautomeric as well as its inductive effect, influence reactivity in *m-* side-chains, although to a less degree than would otherwise occur if the side-chains were otherwise situated. The operation of this second principle may be seen in a number of side-chain reactions, though they are always complicated by the simultaneous presence of the inductive effect, the relay of which to the *meta* position is not of course by any means peculiar to side-chain reactions.

In side-chain reactions of the B type, it is necessary to use the analogy furnished by aromatic substitution reactions in which the replacement of some electronegative group or element in the nucleus is affected by a positive-centre-seeking reagent. As has already been indicated, this side of the picture of aromatic substitution has not been greatly developed, but its essential features are the reversal of the sign of the inductive effect ($+ I$ meaning deactivation and $- I$ activation), and the appearance of an *op*-activating tautomeric effect $- T$. The classification given on page 92 of the previous chapter, is applicable also to side-chain reactions of the B type, after the introduction of modifications relating to the diminished importance of the tautomeric effect, and the ability of this effect to reach *meta* side-chains.

If this classification is compared with that alluded to in connexion with side-chain reactions of the type A ($+ I$, $- I$, $- I + T$, and $+ I + T$), it will be seen that, owing to the radically altered nature of the tautomeric effect, the influence of groups on this kind of nuclear substitution is far from being the complete inverse of their influence on reactivity in the replacement of hydrogen in nuclear substitution. The diminished importance of the tautomeric effect in side-chain transformations, however, leads to what is in a sense a simplification of the theory in that it causes the modifying influence of groups on type B reactivity to be practically the inverse of their effect in side-chain reactions of the A type. This results in a fairly consistent inversion of the type indicated, and on this basis it will be seen that the theory of side-chain reactivity accounts for the series of relations which were formerly explained on the basis of the principle of alternate polarities.

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CHAPTER X

THE THEORY OF TAUTOMERISM

It is well known that the phenomenon of reversible isomeric change to which Laar [1] gave the name of *tautomerism* in his classical memoir of 1885, may occur in two distinct forms in carbon compounds. The first of these and that to which by far the greatest number of examples belong involves the movement of an atom or group accompanied by the appropriate shifting of an unsaturated linkage, while the second, which has been termed " intra-annular " [2] by its discoverers is independent of the movement of an atom or group and is most frequently encountered in the study of aromatic compounds.

With regard to the first of these, the mobile atom most frequently encountered is, of course, hydrogen, and substances of this type were originally classified by Laar into " dyad systems " and " triad systems." The number of examples of dyad mobility is necessarily small and the best-known example is provided by hydrogen cyanide, which is usually represented as an equilibrium between the nitrile and *iso*nitrile forms

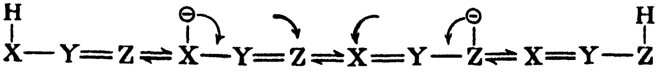
$$[\mathrm{H}]\mathrm{C}{\equiv}\mathrm{N} \rightleftharpoons \mathrm{C}{=}\mathrm{N}[\mathrm{H}].$$

Hamick, New, Sidgwick, and Sutton,[3] however, have recently shown by measurements of the parachors and dipole moments of a number of *iso*nitriles that the *iso*nitrile group has the semi-polar structure $\mathrm{N}\underline{\underline{\rightarrow}}\mathrm{C}$. This reveals at once the identity of the ions derived from the nitrile and isonitrile forms of hydrocyanic acid, $[\mathrm{N}{\equiv}\mathrm{C}]^{\ominus}$, which is evidently the basis for the apparently conflicting evidence with regard to the chemical behaviour of this compound and its salts. The development of the modern electronic theory of tautomerism has been concerned almost exclusively with triad systems, however, and these will therefore be the main subject of this chapter.

Mobile-hydrogen triad systems are generally represented by the formula $[H]X{-}Y{=}Z \rightleftharpoons X{=}Y{-}Z[H]$ and are classified into "symmetrical" and "unsymmetrical" systems, according as to whether X and Z are atoms of the same element or otherwise. A more general expression for the phenomenon of triad mobility is, however, given by $A{-}X{-}Y{=}Z \rightleftharpoons X{=}Y{-}Z{-}A$ where A represents a mobile atom such as hydrogen, or a mobile group such as bromine or acetoxyl.

The moment that a bond is identified with an electronic duplet, it will be seen that the change $X{-}Y{=}Z \longrightarrow X{=}Y{-}Z$ involves the internal displacement of electrons. In tautomeric changes of this type, however, it is necessary to take account not only of the internal movement of electrons but of the external transference of an atom or group in its *ionic* form. The process of reversible isomeric change in such systems is regarded as occurring in three stages: firstly, an atom or group is ionised and dissociates, leaving behind an organic ion in which the charge becomes distributed by electronic displacements of the type characteristic of triad mobility, and lastly, the ion reassociates with the various points at which the electric charge has become localised in the organic ion. On the basis of this, it will be seen that there can be two manifestations of triad tautomerism, in one of which the ion which is externally transferred is a cation, the isomeric change taking place within the organic anion, and the second of which is the converse of this in which the ion transferred is an anion and the isomerising ion is positively charged. Both of these types of triad mobility are now known, and are termed *cationotropic* and *anionotropic* respectively.[4] It will be seen that on the basis of this theory, triad systems of the mobile hydrogen and the mobile metal types are brought into the same group, and the difference in behaviour between systems of the mobile hydrogen and mobile metal type is attributable to the difference in degree of covalency union. Furthermore, on the basis of this theory, the *mobility* of cationotropic systems is seen to depend on the relative stability of the organic ions within which the actual isomeric change takes place, and the *equilibrium* to depend mainly on the stability of the isomeric anions and on the strength of the covalent links by which the cation reassociates with them.

Prototropy.—The cationotropic systems which have been most closely studied are those of the mobile hydrogen type, which are termed *prototropic*, and the general picture for the mobility of which may be given as follows:



the real equilibrium it will be noted being between the two isomeric anions.

This theory, although it is not directly proved, rests on a comprehensive body of evidence, the most important points of which are the following[5]: (i) A parallel exists between the mobility of typical prototropic systems, such as the three-carbon system of indene and the pentad keto-enol system studied by Kon and Linstead, and those properties such as the alkylation and the stability of alkali metal salts to hydrolysis, alcoholysis, and ammonolysis which measure the tendency to ionisation of the mobile hydrogen atom and the stability of the anion. (ii) Mobility runs parallel with the general acid character and is largely independent of the part of the system which is not responsible for acidic properties; the nature of the central atom of the triad being relatively unimportant. Thus the mobility of the amidine system [H]N—C=N $\rightleftharpoons$ N=C—N[H] and the diazoamino system [H]N—N=N $\rightleftharpoons$ N=N—N[H] is of the same order, and a striking similarity exists between the mobility of the systems C[H]—C=C $\rightleftharpoons$ C=C—C[H] and C[H]—N≡C $\rightleftharpoons$ C=N—C[H] when terminated by the same aryl groupings. Furthermore, the mobilities of triad systems terminated by different atoms are in the order of the ionisation sequence of the atoms concerned, *viz.*, HO > HN > HC. (iii) The most effective catalysts for mobile hydrogen tautomerism are alkalis, which act in proportion to the hydrion affinity of their anions, in accordance with the sequence *iso*propoxide > *n*-propoxide > ethoxide > methoxide > hydroxyl.[6] (iv) In triad systems of the type

$$p\text{-R}\cdot C_6H_4\cdot CH_2\cdot CX : CHPh \rightleftharpoons p\text{-R}\cdot C_6H_4\cdot CH : CX\cdot CH_2Ph$$

and

$$p\text{-R}\cdot C_6H_4\cdot CH_2\cdot N : CHPh \rightleftharpoons p\text{-R}\cdot C_6H_4\cdot CH : N\cdot CH_2Ph$$

it has been shown by Shoppee[7] that the most powerful activating groups are the *meta*-directing substituents of aromatic chemistry and that the facilitation of prototropy runs parallel with the electron affinity of the group R as measured by the dipole moment of the corresponding substituted benzene derivative $C_6H_5\cdot R$.

A particularly interesting example of this picture of mobile hydrogen tautomerism is provided by phenylnitromethane. The anion of this compound is stable in alkaline aqueous solution and Hantzsch has shown that its association with hydrion can be followed up by conductivity measurements, and the reaction was therefore subjected to a detailed study by Branch and Jaxon-Deelman[8] a few years ago. It was observed by the American investigators that when a dilute aqueous methyl alcoholic solution of the sodium salt of phenyl*iso*nitromethane was mixed with an equivalent of hydrochloric acid, the conductivity fell away in such a manner as to show that after the initial disturbance, due to the rapid formation of a relatively weak electrolyte in equilibrium with its ions, that one of these ions became involved in a slow unimolecular change leading to the formation of undissociated acid. The comparatively weak electrolyte is evidently the *aci* form of the nitromethane (I), and it was shown that it is the ion of this (II), which undergoes slow unimolecular change because the concentrations of (I) and (II) do not bear a constant relation to each other since the fraction ionised increases as the *aci* form is destroyed. The actual isomerisation between the two ions, which can be reversed under other conditions, is not essentially reversible in this case because it is succeeded by rapid and complete ionic association with the production of the *pseudo* acid itself (IV).

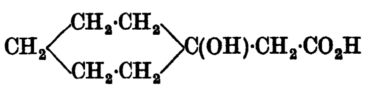
$$\begin{array}{rcl}
\text{(I) } \mathrm{Ph\cdot CH:NO\cdot OH} & \underset{\text{(rapid)}}{\rightleftharpoons} & \overset{\oplus}{\mathrm{H}} + \mathrm{Ph\cdot CH:NO\cdot}\overset{\ominus}{\mathrm{O}} \text{ (II)} \\
 & & \qquad\quad \upharpoonleft\!\downharpoonright \text{ (slow)} \\
\text{(IV) } \mathrm{Ph\cdot CHH\cdot NO_2} & \underset{\text{(rapid)}}{\rightleftharpoons} & \mathrm{H}^{\oplus} + \mathrm{Ph\cdot C}\overset{\ominus}{\mathrm{H}}\mathrm{\cdot NO_2} \text{ (III)}
\end{array}$$

It is the stability of the covalent link C—H formed in the last reaction III ⟶ IV as compared with the ready dissociation of the O—H link in the reaction II ⟶ I, which is responsible for the whole series of changes in the direction I ⟶ IV.

During the last few years, considerable attention has been devoted by Kon and Linstead[9] to the prototropy of the so-called three-carbon system present in unsaturated acids of the type studied by Fittig, and in unsaturated open-chain and cyclic ketones containing a hydrogen atom and a double bond in the appropriate position. In so far as the enolic intermediate can be neglected in the system $\mathrm{C:C{\cdot}C[H]{\cdot}C:O \rightleftharpoons C:C{\cdot}C:C{\cdot}O[H] \rightleftharpoons C[H]{\cdot}C:C{\cdot}C:O}$ there is some justification in regarding the tautomeric change as belonging to the three-carbon type $\mathrm{C[H]{\cdot}C:C \rightleftharpoons C:C{\cdot}C[H]}$ present in indene and the trialkylpropenylammonium salts studied by Ingold and Rothstein.[10] Since interconversions of this type occur in the presence of a large concentration of hydroxyl or alkoxyl ions and quantities of saturated hydroxy or alkoxy acids are frequently formed under the conditions of the interconversion, it has more than once been suggested that such $\alpha\beta$–$\beta\gamma$ changes are not tautomeric in character but are produced by the preliminary addition of water or alcohol, followed by elimination of the addendum in a new direction. That there is no justification for this view was shown by the fact that the phenylbutenoic acids (V) and (VI) come rapidly into equilibrium, and continued treatment with alkali merely increases the amount of the hydroxy acid without affecting the proportion of the isomerides.

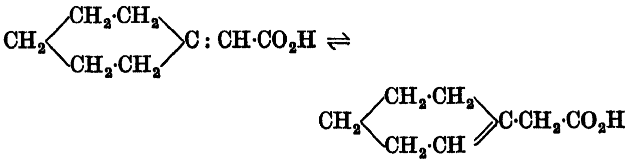
$$\text{(v)}\quad \mathrm{Ph{\cdot}CH_2{\cdot}CH:CH{\cdot}CO_2H \rightleftharpoons Ph{\cdot}CH:CH{\cdot}CH_2{\cdot}CO_2H}\quad \text{(vi)}$$

Furthermore, in the *cyclo*hexane acetic acid series, the hydroxy acid (VII) is formed too slowly and loses water too slowly to be the intermediate product in the interconversion of the isomerides (VIII) and (IX).[11]



(VII)

(VIII)



(IX)

Substances exhibiting retarded mobility of this type are therefore of considerable interest in that their stability enables the proportion of the tautomers at equilibrium to be determined, and valuable data of the effect of structure on equilibrium in such compounds has been collected by Kon and Linstead, which is of considerable interest from the point of view of the ionotropic theory of tautomerism. Thus γ-substitution of a methyl group for hydrogen in the three-carbon system causes a displacement of the equilibrium in the direction of the $\beta\gamma$-form, due to the slight negative polarity conferred on the γ-carbon atom which decreases its toleration for the negative charge which has to be distributed between the α- and γ-carbon atoms when the mobile proton leaves the system. The substitution of methyl for hydrogen in the α-position has the opposite effect, as is shown by a comparison of the pentenoic and methylpentenoic acids; the proportions of $\alpha\beta$-form present at equilibrium being [12]:

γ-Methylpentenoic Acid	Pentenoic Acid	α-Methylpentenoic Acid
5·6% $\alpha\beta$-form	75·4% $\alpha\beta$-form	80·7% $\alpha\beta$-form

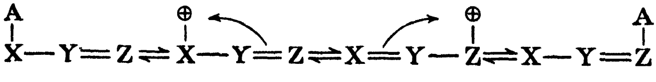
Anionotropy.—The discovery of this type of triad mobility which has been named "anionotropic" is a comparatively recent event and dates from Burton and Ingold's [13] investigation of the mobility of the three-carbon system containing a mobile hydroxyl group:

$$\mathrm{C[OH]\cdot CH : CHX \rightleftharpoons C : CH\cdot C[OH]}.$$

It was observed by these investigators that in the series

$$p\text{-}\mathrm{R\cdot C_6H_4\cdot CH[OH]\cdot CH : CHPh} \rightleftharpoons p\text{-}\mathrm{R\cdot C_6H_4\cdot CH : CH\cdot CH[OH]\cdot Ph}$$

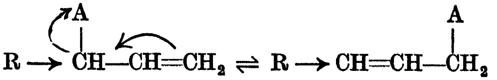
the mobility of the hydroxyl group [OH] increases in the order $\mathrm{R = Cl > R = Me > R = H}$, in accordance with the *o*-*p*-orienting influence of these groups in ordinary aromatic substitution. On the basis of this and certain other observations made with regard to the addition of bromine to conjugated systems of the butadiene type, it was suggested by these authors that the mobility of systems of this type in which the mobile group is known to be stable in its anionic form might be represented by a picture which is essentially the converse of that which has been suggested for cationotropic systems:



$$\overset{\overset{A}{|}}{X}-Y=Z \rightleftharpoons \overset{\overset{\oplus}{|}}{X}-Y=Z \rightleftharpoons X=Y-\overset{\overset{\oplus}{|}}{Z} \rightleftharpoons X-Y=\overset{\overset{A}{|}}{Z}$$

On the basis of this, the three main factors facilitating tautomeric change of this type should be: (i) the stability of the group A in its anionic form $A^{\ominus}$ as indicated by the strength of the acid HA, (ii) the presence of external cations, or, in their absence, the ionising power of the medium as indicated by its dielectric constant, and (iii) the capacity of the system to supply electrons to the ionising centre and so facilitate the separation of A as a negative ion.

With regard to the three-carbon system (X ⇌ XI), it is found that when R is phenyl and the mobile group A is hydroxyl, mobility is small because α-phenylallyl and cinnamyl alcohols are obtainable separately, and each can be esterified without undergoing change of structure.



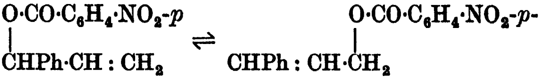
$$\text{(x)}\quad R \rightarrow \overset{A}{\overset{|}{C}}H{-}CH{=}CH_2 \rightleftharpoons R \rightarrow CH{=}CH{-}\overset{A}{\overset{|}{C}}H_2 \quad \text{(xi)}$$

The acetyl and *p*-nitrobenzoyl esters (A = O·CO·Me and ·O·CO·C_6H_4, NO_2-*p*-), on the other hand, undergo smooth interconversion in the direction of X → XI in solvents such as chlorobenzene, acetic anhydride, and benzonitrile. Finally, the bromohydrocarbons (A = Br) are so mobile that only one of them (XI, R = Br) can be isolated. Mobility therefore runs parallel with the stability of the anion $\overset{\ominus}{A}$:—Br > O·COMe > ·OH. With regard to the effect of the polar field of the solvent on the mobility of the system, it has been found that for the same example, the rate of conversion at constant temperature varies in the order: benzonitrile > chlorobenzene > P-xylene in accordance with the corresponding dielectric constants of these solvents which are approximately 26, 6, and 2 in the order named. Finally, as has already been mentioned, it has been found for the three-carbon anionotropic system terminated at one end by groups *p*-X·C_6H_4- that the mobility of the system increases in the order

$$X = Cl > X = Me > X = H$$

in accordance with the *o*-*p*-orienting sequence Cl > Me > H observed in benzene substitutions.

The fact that the group A leaves the three-carbon system as an anion and returns to it as an anion was proved by Burton in 1928 by an examination of the isomerisation of the system (XII ⇌ XIII) in the presence of soluble acetate.

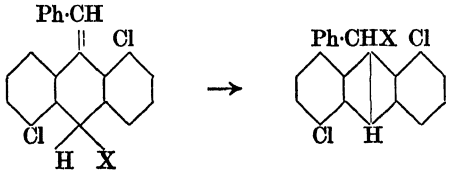


$$\underset{\text{(xii)}}{\overset{O\cdot CO\cdot C_6H_4\cdot NO_2\text{-}p}{\overset{|}{C}HPh\cdot CH:CH_2}} \rightleftharpoons \underset{\text{(xiii)}}{CHPh:CH\cdot\overset{O\cdot CO\cdot C_6H_4\cdot NO_2\text{-}p\text{-}}{\overset{|}{C}H_2}}$$

If the *p*-nitrobenzoyloxy group migrates as the *p*-nitrobenzoate ion, and in so doing definitely separates from the cation within which the isomeric change takes place, acetate ions should be able to compete with it during its return, and a considerable proportion of the material might be expected to be recovered in the form of the acetoxyhydrocarbon. This is actually what happens, a considerable proportion of the acetohydrocarbon being isolable when the isomerisation is carried out in the presence of tetramethylammonium acetate.[14]

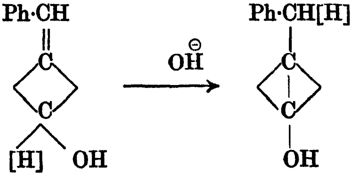
Some interesting examples of anionotropy in cyclic systems have also been discovered by Barnett, Matthews, and Cook [15] in the anthracene series. These transformations are of the type (XIV ⟶ XV), where the mobile group X is hydroxyl, acetoxyl, etc., and are catalysed by strong acids, and are clearly concerned with the lability of X arising from the 5-chlorosubstituent and with the fact that the replacement of the *meso* hydrogen atom by a phenyl group tends to stabilise the form (XV).

(xiv)

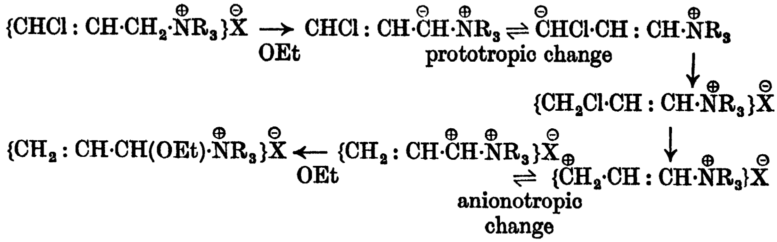


(xv)

Particular interest attaches itself to the case in which X is hydroxyl, because here both transannular anionotropy and prototropy are possible, in accordance with which it has been found that whereas the hydroxy derivative (XIV, X = OH) undergoes the usual anionotropic change under the action of strong acids, an analogous prototropic change to the anthranol is produced by the catalytic action of strong alkalis:



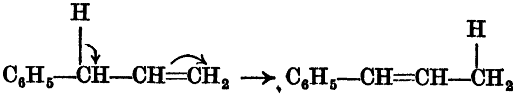
An interesting case in which both anionotropy and prototropy occur in the same three-carbon system was described by Ingold and Rothstein.[16] It was discovered by these investigators that alcoholic sodium ethoxide readily converts a trialkyl-γ-chloroallylammonium salt into the trialkyl-α-ethoxyallylammonium salt. This curious result is due to a prototropic change induced by the ethoxide ions, followed by a reaction involving anionotropic rearrangement:



$$
\begin{aligned}
&\{\mathrm{CHCl:CH{\cdot}CH_2{\cdot}\overset{\oplus}{N}R_3}\}\overset{\ominus}{\mathrm{X}} \xrightarrow[\mathrm{OEt}]{} \mathrm{CHCl:CH{\cdot}\overset{\ominus}{C}H{\cdot}\overset{\oplus}{N}R_3} \underset{\text{prototropic change}}{\rightleftharpoons} \mathrm{\overset{\ominus}{C}HCl{\cdot}CH:CH{\cdot}\overset{\oplus}{N}R_3}\\
&\downarrow\ \{\mathrm{CH_2Cl{\cdot}CH:CH{\cdot}\overset{\oplus}{N}R_3}\}\overset{\ominus}{\mathrm{X}}\ \downarrow\\
&\{\mathrm{CH_2:CH{\cdot}CH(OEt){\cdot}\overset{\oplus}{N}R_3}\}\overset{\ominus}{\mathrm{X}} \xleftarrow[\mathrm{OEt}]{} \{\mathrm{CH_2:CH{\cdot}\overset{\oplus}{C}H{\cdot}\overset{\oplus}{N}R_3}\}\overset{\ominus}{\mathrm{X}}_{\oplus} \underset{\substack{\text{anionotropic}\\ \text{change}}}{\rightleftharpoons} \{\mathrm{\overset{\oplus}{C}H_2{\cdot}CH:CH{\cdot}\overset{\oplus}{N}R_3}\}\overset{\ominus}{\mathrm{X}}
\end{aligned}
$$

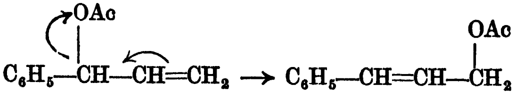
The final product being an ethoxy allyl derivative and not a chloro compound, due to the fact that the ethoxide ion has a greater co-ordinating power than the chlorine ion, and is furthermore present in considerable excess.

A curious feature of the phenyl group in relation to its effect on promoting tautomeric mobility is that it not only activates *prototropy* in three-carbon systems as in the conversion of allylbenzene into propenylbenzene:



$$\mathrm{C_6H_5{-}\overset{\overset{\displaystyle H}{|}}{C}H{-}CH{=}CH_2 \longrightarrow C_6H_5{-}CH{=}CH{-}\overset{\overset{\displaystyle H}{|}}{C}H_2}$$

but it also promotes the *anionotropic* conversion of α-phenylallyl esters into cinnamyl esters:

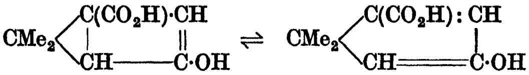


$$\mathrm{C_6H_5{-}\overset{\overset{\displaystyle OAc}{|}}{C}H{-}CH{=}CH_2 \longrightarrow C_6H_5{-}CH{=}CH{-}\overset{\overset{\displaystyle OAc}{|}}{C}H_2}$$

Ingold[17] explains this by the suggestion that the main polar effect of the phenyl group is a tautomeric one of either sign ($\pm T$), which can therefore act either by attracting or releasing electrons according to the *momentary* requirements of the attacking reagent. In the cases mentioned, the attacking reagent is the catalyst or solvent molecule the electric field of which assists in the removal of mobile cation or anion, and the phenyl group probably first facilitates ionisation, and then absorbs part of the charge produced on the α-carbon atom, leaving the γ-carbon atom to receive the detached ion.

This view of the curious property of the phenyl group in activating both prototropic and anionotropic changes by tautomeric displacements of either sign called into being at the requirements of the system has considerable bearing on the theory of free radicals of the type of triphenylmethyl, which is discussed in Chapter XII.

Intra-Annular Tautomerism.—The application of the electronic theory to valency tautomerism, such as occurs in certain di*cyclo*pentanone derivatives:



is easily understood; the positive charges simultaneously produced by the movement of the double linking, being neutralised by the corresponding movement of the second double bond, such that ions do not separate in the process.

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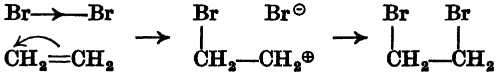
CHAPTER XI

CONJUGATION AND THE IONOTROPIC THEORY

One of the most valuable applications of the ionotropic theory of tautomerism outlined in the last chapter, is to the problem of the addition of bromine and hydrogen to conjugated compounds of the butadiene type. Although Thiele's writings make it clear that he originally intended his hypothesis to imply universal 1 : 4-addition, it is well known that this position can no longer be maintained, and that the Thiele hypothesis even with its later modifications has by no means the diagnostic value which it was originally supposed to possess. The application of the principles of prototropy and anionotropy to these reactions has shed new light on the whole subject, and provides a rational explanation of most of the difficulties encountered in earlier investigations.

The isomerisation $A{-}x{-}y{=}z \rightarrow x{=}y{-}z{-}A$ may be regarded as the intramolecular addition of the addendum $A{-}x$ to the unsaturated complex $y{=}z$. We can suppose that the addition of the two parts does not occur simultaneously, but that x first becomes detached and then adds to y, and then at a later stage A adds to z, and furthermore that the two parts of the addendum add as ions of opposite sign. If x acting as an anion uses its own electrons in adding to y, then A acts as a cation and unites with electrons belonging to z; representing thereby a case of cationotropy. Conversely, if x acts as a cation, then A will act as an anion, and process will be the anionotropic type.

On the basis of this, the addition of bromine to ethylene may be pictured as a two-stage heteropolar process the first stage of which consists in the addition of positively polarised bromine to the olefine :



$$\begin{array}{c} Br\rightarrow Br \\ CH_2{=}CH_2 \end{array} \rightarrow \begin{array}{cc} Br & Br^{\ominus} \\ | & \\ CH_2{-}CH_2^{\oplus} & \end{array} \rightarrow \begin{array}{cc} Br & Br \\ | & | \\ CH_2{-}CH_2 & \end{array}$$

If, in this reaction, it is possible to divert the second stage by carrying out the reaction in the presence of an anion calculated to compete with the bromide ion in co-ordinating with bromoethyl cation, then two products should be obtained, and this is actually the case. Thus it was shown by Francis in 1925,[1] that if the reaction between ethylene and bromine is carried out in the presence of an aqueous solution of sodium nitrate, a considerable proportion of the compound $\mathrm{Br{\cdot}CH_2{\cdot}CH_2{\cdot}ONO_2}$ is formed alongside the ethylene bromide in accordance with the mechanism outlined above. An immediate consequence of this is that the principle of anionotropy can at once be applied to the problem of the addition of bromine to conjugated hydrocarbons.

The initial product of addition of bromine to butadiene, for instance, may be what can be termed the ions of the 1 : 2-dibromide :

$$\mathrm{CH_2{\cdot}CH : CH{\cdot}CH_2} \longrightarrow \overset{\ominus}{\mathrm{Br}} + \mathrm{Br{\cdot}CH_2{\cdot}\overset{\oplus}{C}H{\cdot}CH : CH_2}.$$

If, however, conditions are present which favour ionisation, the cation will be that of an anionotropic system whose charge will undergo distribution in accordance with the capacity for electron release of $\mathrm{Br{\cdot}CH_2}$ and hydrogen respectively, leading to the production of the 1 : 4-dibromide in a quantity predominating over the proportion of the 1 : 2-dibromide :

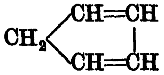
$$\overset{\ominus}{\mathrm{Br}} + \mathrm{BrCH_2{—}\overset{\oplus}{C}H{\cdot}CH : CH{—}H} \rightleftharpoons \mathrm{BrCH_2{—}CH : CH{\cdot}\overset{\oplus}{C}H} + \mathrm{Br}$$

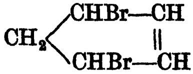
Actually, it has been shown by Farmer, Lawrence, and Thorpe [2] that under conditions which are readily recognised as non-ionising, that the bromination product is the 1 : 2-dibromide, whilst in ionising solvents, a mixture of the 1 : 4- and 1 : 2-dibromo-addition products is obtained in the proportion of about two to one in favour of the former. Farmer and his collaborators [3] have also shown that high proportions of the 1 : 4-dibromo-addition products are also obtained in the bromination of $\alpha\delta$- and $\alpha\gamma$-dimethylbutadiene (I and II respectively), and that the proportion of 1 : 4-dibromide (IV) obtained in the bromination of *cyclo*pentadiene (III) is increased when the solvent is changed from hexane to chloroform.

(I) $\mathrm{CHMe : CH{\cdot}CH : CHMe}$

$\mathrm{CHMe : CH{\cdot}CMe : CH_2}$ (II)

(III)





(IV)

The addition of bromine to conjugated systems of this type can therefore be represented by means of the general scheme :

$$\begin{tikzcd}
\text{Reagents} \arrow[r] & \text{Ions of 1 : 2-Dibromide} \arrow[r, shift left] \arrow[d, shift left] & \text{1 : 2-Dibromide} \arrow[l, shift left] \\
& \text{Ions of 1 : 4-Dibromide} \arrow[r, shift left] \arrow[u, shift left] & \text{1 : 4-Dibromide} \arrow[l, shift left]
\end{tikzcd}$$

It will be observed that this theory of halogen additions assumes that the initial attack of the halogen molecule is at the α-carbon atom of the butadiene, leading to the entrance of the halogen cation at this point. This prior attack at the α-carbon atom is a necessary supposition so far as the production of the 1 : 4-dibromo-addition compound is concerned, but there is a possible alternative conception with regard to the formation of the 1 : 2-isomer, namely, that the attack of the halogen commences at the β-carbon atom, and that the latter reaction is only completed by the attachment of the halide residue to the α-carbon atom of the butadiene group.

This point has been settled by Ingold and Smith [4] by an examination of the addition of iodine monochloride to butadiene, on the basis of the fundamental assumption that the location of the iodine atom in an iodine monochloride addition product marks the point of commencement of the reaction. Farmer, Lawrence, and Thorpe observed that the product of the addition of two bromine atoms to butadiene in chloroform at − 15° contained 37% of the 1 : 2-dibromide. It was found by Ingold and Smith that the product of the action of iodine monochloride on butadiene in methylene chloride at − 35° consisted mainly of the 1 : 4-addition compound (V), accompanied by 22% of the 1 : 2-isomeride (VI), there being no evidence of the production of the other possible 1 : 2-addition product (VII) in any significant quantity.

(V) $CH_2I{\cdot}CH:CH{\cdot}CH_2Cl$ $CH_2I{\cdot}CHCl{\cdot}CH:CH_2$ (VI)

$CH_2Cl{\cdot}CHI{\cdot}CH:CH_2$ (VII)

This experiment therefore indicates that the point of attack of the halogen in a butadiene is the α-carbon atom, in agreement with the anionotropic theory of the addition of bromine to conjugated systems we have just outlined.

This analogy which has been traced between the addition of bromine and anionotropy finds its counterpart in hydrogen addition and prototropy.[5] The reduction of an olefine linking may be regarded as a three-stage process consisting of the following stages: (i) First, the unsaturated molecule, polarised in the electric field at the surface of the metal, extracts a proton from the aqueous or alcoholic solution in which the reduction is carried out; this proton becomes attached to the α-carbon atom which most readily tolerates the negative polarisation charge developed prior to co-ordination—the process being regarded as reversible and as almost completely dependent for its left to right progress on a rapid metamorphosis of the unstable complex cation:

$$\overset{\curvearrowright}{\mathrm{C{=}C}}\longrightarrow\mathrm{X} + \overset{\oplus}{\mathrm{H}} \rightleftharpoons \overset{\oplus}{\mathrm{C}}\mathrm{—CH—X};$$

(ii) The cation possesses an electron sextet at the β-carbon atom and its electron affinity exerted in the region of the metallic surface locally breaks down the electrostatic potential barrier inhibiting the escape of metallic electrons, and the successive absorption of the two electrons which are necessary for converting the sextet into the stable octet converts the cation into an anion

$$\overset{\ominus}{\mathrm{C}}\mathrm{—CH—X};$$

(iii) Finally, the anion extracts a second proton from the solution giving

$$\mathrm{C—H{\cdot}CH{\cdot}X}.$$

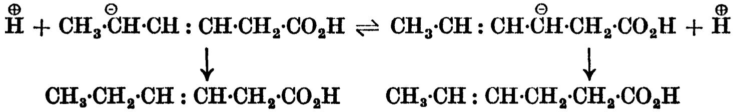
It may be noted that the first stage shows that this picture offers an immediate explanation of the well-known fact that the only aliphatic olefinic acids which are reducible by metals in aqueous media are the $\alpha\beta$-unsaturated acids, and that furthermore the possession of this type of structure is but one of the ways in which an olefinic substance can satisfy the more general theoretical requirement that for facile reduction, at least one ethenoid carbon atom has to be attached to an electron sink.

The application of these principles can readily be illustrated by means of the reduction of crotonic acid; here the tendency to polarisation produced by the electron affinity of the carboxyl group cannot, of course, come to fruition in ordinary circumstances, because the process would cause the production of an unshared duplet at the α-carbon atom and a sextet at the β-carbon atom. When, however, a source of hydrogen ions and electrons is present as in reduction by metals, polarisation and the addition of ($H^{\cdot} + 2e$) can proceed to produce an anion

$$\mathrm{CH_3{\cdot}\overset{\ominus}{C}H{\cdot}CH_2{\cdot}CO_2H}$$

which is the counterpart of the bromoethyl cation in the bromination of ethylene, which by taking up a further proton yields butyric acid.

In the reduction of a conjugated compound of the type of sorbic acid, the anion formed in the first stage of the reaction is the anion of a prototropic system, possessing a distributable charge, leading to the final combination of proton in two positions:



$$\begin{tikzcd}[column sep=small] \overset{\oplus}{H} + CH_3\cdot\overset{\ominus}{C}H\cdot CH : CH\cdot CH_2\cdot CO_2H \arrow[r, leftrightharpoons] \arrow[d] & CH_3\cdot CH : CH\cdot\overset{\ominus}{C}H\cdot CH_2\cdot CO_2H + \overset{\oplus}{H} \arrow[d] \\ CH_3\cdot CH_2\cdot CH : CH\cdot CH_2\cdot CO_2H & CH_3\cdot CH : CH\cdot CH_2\cdot CH_2\cdot CO_2H \end{tikzcd}$$

Actually it has been shown by Evans and Farmer[6] and by Burton and Ingold[5] that, contrary to the older supposition of the formation of a homogeneous 1 : 4-addition compound in the metallic reduction of sorbic acid, substantial amounts of the 1 : 2-dihydro derivative are also produced, in accordance with the theory just outlined, which indicates that not only should the latter isomeride be produced, but it should predominate, although only slightly, over the 1 : 4-dihydro compound.

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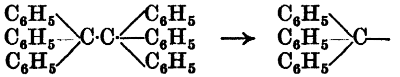
CHAPTER XII

TRIPHENYLMETHYL AND ITS DERIVATIVES

Another interesting result of the development of the ionotropic theory of tautomerism developed in Chapter X is the fresh light which it has thrown on the problem of the existence and stability of free radicals of the triphenylmethyl class. Before dealing with this, however, it appears desirable to give a brief historical summary of the salient points in connexion with the development of the chemistry of these compounds.

It will be recalled that the dissociation of hexaphenylethane (I) into a coloured, highly reactive, *free radical* triphenylmethyl (II) was first claimed by Gomberg [1] at the beginning of the present century, but whilst the experimental work was still incomplete, quinonoid formulæ, isomeric with that of hexaphenylethane were suggested by Jacobsen [2] as an alternative to the conception of a tervalent carbon atom.

(I)



(II)

Two or three years later, Schmidlin's [3] examination of the equilibrium between the reactive and unreactive entities in solutions of hexaphenylethane and Schlenk's [4] discovery of the definite dissociation of other hexa-arylethanes, definitely established the reversible formation of coloured reactive free triaryl radicals throughout the series. About the same time, however, Gomberg [5] obtained definite proof of the quinonoid isomerisation of certain *p*-halogenotriphenylmethyl halides and postulated for the general case, a picture of dissociation and quinonoid isomerisation of both the associated and dissociated forms of triphenylmethyl.[6] Some years later, it was discovered by Gomberg [7] that the absorption spectra of the dissociated forms of hexaphenylethanes are different in non-ionising and ionising solvents, indicating the existence of both triarylmethyl ions and neutral triarylmethyl radicals. In 1924, it was pointed out by Ingold[8] that much of the confusion surrounding the whole subject of triarylmethyls could be avoided by recognising the individuality of the three triphenylmethyls formed by the neutral and ionic dissociation of hexaphenylethane as follows:

$$2Ph_3\overset{\odot}{C} \rightleftharpoons Ph_3C—CPh_3 \rightleftharpoons Ph_3\overset{\oplus}{C} + Ph_3\overset{\ominus}{C}$$

the neutral radical being formed alone in non-ionising solvents and the two ions together in ionising solvents; but that the cation alone is present in the solutions of triphenylmethyl chloride in liquid sulphur dioxide which have received so much attention. It was also suggested by Ingold that the anion exists alone in solutions of potassium triphenylmethide in liquid ammonia:

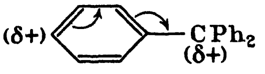
$$Ph_3CCl \rightleftharpoons Ph_3\overset{\oplus}{C} + \overset{\ominus}{Cl}$$

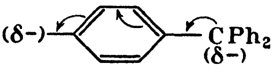
$$Ph_3CK \rightleftharpoons Ph_3\overset{\ominus}{C} + \overset{\oplus}{K}$$

Since then, the existence of the triphenylmethyl anion in the ammonia solution has been confirmed by Kraus and Rosen,[9] and some of its reactions have been investigated.

On the basis of the recognition of two types of triphenylmethyl ion in addition to the neutral triphenylmethyl radical, most of the puzzling features of the group disappear. It may be noted that Gomberg's evidence of quinonoid isomerisation applies only to the positive triphenylmethyl ion, which might be expected to exhibit this phenomenon since it is the cation of an anionotropic system and has therefore a distributable charge (III). This does not imply that similar quinonoid transformations cannot occur in the triphenylmethyl anion, which can probably exhibit the reverse type of electron displacement (IV), but merely that suitable experiments of this type have not so far been undertaken with respect to the negative ion.

(III)





(IV)

It is therefore seen that the quinonoid isomerisation of dissociated forms presents no real difficulty when the subject is approached from this standpoint. The fundamental question with which we are concerned is, however, the reason as to why the original dissociation occurs at all.

It has already been pointed out that aryl groups possess the power of activating both prototropic and anionotropic changes; that is to say that they confer on an attached atom the power of tolerating an electric charge of either sign:

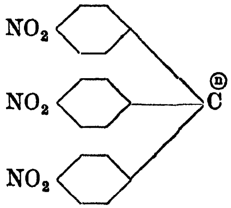
$$\mathrm{Ar}-\overset{\oplus}{\mathrm{C}}\mathrm{H{\cdot}CH:CH}-\mathrm{Ar'} \qquad \mathrm{Ar}-\overset{\ominus}{\mathrm{C}}\mathrm{H{\cdot}CH:CH}-\mathrm{Ar'}$$

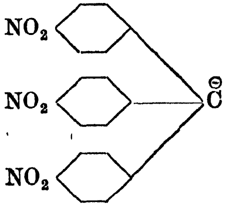
The reason for this is that they evidently contain an available mechanism for the extensive distribution of an ionic charge of either sign originally present in an attached atom. This property is clearly what is required to account for the dissociation of hexaphenylethane into triphenylmethyl cation and triphenylmethyl anion and the ionisation of triphenylmethyl chloride and the potassium derivative of triphenylmethyl. In accepting this as the explanation of these ionisations, it must be assumed that in the hexa-arylethane series, the accumulation of aryl groups renders their effect *quantitatively* sufficient to produce that thermodynamic stability in the two triarylmethyl ions which is implied by such equilibria. From this it is but a short step to infer that the same causes as induce stability in the triphenylmethyl ions would induce corresponding stability in the neutral triphenylmethyl radical. Thus, the methyl carbon atom (electron septet) in the neutral triphenylmethyl radical is simultaneously affected by the two factors, normally inducive of instability, which are respectively identical in type with those present in the two triphenylmethyl ions, namely, the incompleteness of the electron octet (this applies also to the triphenylmethyl cation), and the incompleteness of the electron sharing (which applies also to the negative ion), and a system of groups which can successfully combat both these factors of instability separately can also deal with them together. The stabilisation of the neutral triphenylmethyl radical can therefore be briefly described as electron release from the aryl groups partly repairing the disrupted octet, and incidentally, the disrupted duplet; the unshared pair thus partly formed, being partly shared with the aryl groups.

One consequence of this hypothesis is that polynuclear aromatic systems should act more powerfully than phenyl in promoting the dissociation of hexa-arylethanes, that is to say, in stabilising the free radical, because those rings of a polynuclear group which are more distant from the ethane carbon atom will act as an additional charge-absorbing mechanism, and therefore assist the nearer ring in both its functions of electron release and re-absorption. This is the reason why the diphenylyl derivatives possess greater stability than the simple triphenylmethyl radical. Furthermore, the less restricted the internuclear electron-path, the more pronounced will be the effect of the more distant nuclei.

Another important deduction follows from the fact that an alkyl cation is always more stable than the corresponding alkyl anion, for it is assumed that stability in a neutral radical is dependent on the presence of a condition the efficacy of which is indicated by its ability to stabilise not only the corresponding cation but also the anion. It would be expected therefore that the introduction of a substituent calculated to increase the stability of the anion by attracting electrons would also increase the stability of the neutral radical. An interesting confirmation of this is provided by the free radical *pp′p″*-trinitrophenylmethyl (V), which was isolated by Zeigler and Boye [10] in 1927. The effect of the three semipolar double bonds is so striking that the anion (VI)

(V)

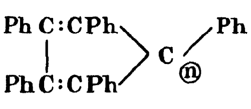




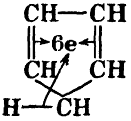
(VI)

can exist undecomposed even in alcohol, and the neutral radical possesses so little tendency to associate that it can be isolated in the free state in deep-green crystals.

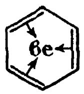
Pentaphenylcyclopentadienyl (VII) affords another illustration of the same phenomenon.[11] The *cyclo*pentadiene ring itself (VIII) possesses considerable electron affinity which is usually ascribed to its tendency to appropriate the two electrons necessary to complete the sextet which is responsible for the stability of benzene (IX) and other aromatic rings.[12]



(VII)



(VIII)



(IX)

The result of this and tetraphenylation of the five-membered ring is sufficient to permit the isolation of the free radical (VII) in reddish-violet crystals which show no tendency towards association·

Recently, Pauling and Wheland have applied the quantum-mechanical method of calculation [13] of resonance energy to the problem of free hydrocarbon radicals [14] and have shown that this leads to values for the dissociation energies of various substituted ethanes which are in excellent qualitative, and even semi-quantitative, agreement with the results of experiment. In doing this, however, they have had to introduce two important simplifications into the method of making calculations of this type to which reference may be made. In the first place, they have neglected all excited states of the molecule, whose contribution to the total energy of the system is comparatively small. Secondly, they have allowed for the odd and therefore unpaired electron present in the free radical by introducing a " phantom orbit " with an accompanying " phantom electron " with which the odd electron of the hydrocarbon radical is paired in making the calculation.

Actually, however, the theory of stability of free radicals which has been developed in this way by these investigators is mainly a refinement of the theory of Burton and Ingold already discussed, for which it provides a wave mechanical basis.

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